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THERMAL DEWATERING OF LIGNITE
PHASE III
FINAL REPORT

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EXECUTIVE SUMMARY

Lignite and peat can be dried by thermal dewatering, a process which involves heating the fuel at a high temperature under a steam pressure greater than the saturated vapour pressure of water at that temperature. Chemical reactions occur and a large portion of the water contained in the pores of the fuel is expelled as liquid water. Energy savings can be realized over evaporative drying processes since there is no vapourization of the water that is removed.

In Phases I and II of this project, thermal dewatering was evaluated on several lignite and peat samples at temperatures up to 350°C. The amount of moisture removed increased with temperature, with reductions of up to 75 percent in moisture content (34 percent moisture coal dried to 9 percent moisture product) being attained. Preliminary studes also indicated that thermal dewatering under oil was more effective than regular dewatering at temperatures up to 250°C. In addition, thermal dewatering under steam and/or mixtures of H_2/CO gave dry products which readily readsorbed water.

Phase III of this project extended the temperature range of the experiments up to 400°C and investigated variables such as retention time, increased rates of heating and cooling, extent of trace element removal, effect of particle size and effect of dewatering under heavy and light oils. Lignites from three geographical areas of Canada (Estevan, Saskatchewan; Coronach, Saskatchewan; and Onakawana, Ontario), as well as one peat sample (Garrick, Saskatchewan), were thermally dewatered in Phase III.

The equilibrium moisture values (moisture level after exposure to 97 percent humidity for 72 hours) obtained in Phase III for the dewatered products were as low as, or lower than those obtained in Phases I and II of this project. However, the measured moisture contents of the thermally dewatered Saskatchewan lignites were somewhat higher than those measured in Phases I and II. The extent of weathering of the coal may affect the final moisture contents.

The equilibrium moisture values and the moisture contents decreased with increasing temperature. An optimum balance between extent of dewatering and resulting steam pressures is obtained for a dewatering temperature between 300°C and 350°C. At these temperatures, residence times in the order of 15 minutes are required.

The extent of dewatering increased with increasing particle size for Onakawana lignite while the opposite trend was seen for the Estevan lignites.

Thermal dewatering under heavy oil was very effective, but only when dry oil was used, and oil losses were high.

Removal of sodium during the dewatering process resulted in products which should generate less slagging and fouling problems in the boilers.

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1.0 INTRODUCTION

Saskatchewan has large deposits of lignite coal, about 7 billion tonnes measured or inferred, and 27 billion tonnes indicated (Irvine et al., 1978). A major problem in utilization of these deposits is that they contain large amounts of moisture (30 -50 percent).

Development of a process for reduction of lignite moisture and sodium will allow more efficient and environmentally acceptable utilization of Canadian lignites. It will enhance the commercial value of the lignite and make it a more attractive fuel for boilers.

The application of beneficiated lignites will bring about reduction of transportation and handling costs on an available energy unit basis. Combustion of beneficiated lignites will require a smaller boiler size for a given boiler output, hence reducing the capital component in the cost of a new power grid. Lower moisture contents of beneficiated lignites will result in decreased stack losses and increased boiler efficiency. Ignition problems associated with higher moisture contents are absent in the combustion of low moisture, low sodium lignites. Problems associated with high sodium contents of Saskatchewan lignites such as fluxing of mineral matter and depositing of ash on heat exchanger areas can be prevented by using a low moisture, low sodium lignite.

A number of methods have been developed to dry lignite or brown coals including evaporation or air-drying. These methods are effective for high grade (bituminous) coals, when only small amounts of water have to be

removed (e.g. after washing) (Leonard, 1979, Chapter 13). This process has also been tested on lignites (Cooley, 1961; Falconer, 1977; Grant, 1978). A large amount of energy is required to evaporate the moisture, and the process tends to produce a large amount of dust as well as a highly friable product which is susceptible to spontaneous combustion.

In the Fleissner process (Oppelt et al., 1955) lignite is heated to about 225°C using saturated steam, at up to 2.6 MPa. Some water is removed as liquid, the remainder as steam with steam consumption of 0.6 to 0.85 kg/kg of water removed. Since removal of water as liquid does not require vapourization the energy needed is about 60 percent of that required for conventional air-drying. The process has been considered uncompetitive when coal in the form of lumps is not required, as in the case of pulverized fuel boilers (Mitchell et al., 1967), because of the high cost of the batch operation of the autoclaves.

A high-temperature, high pressure beneficiation process has been developed by Koppelman (Parkinson, 1978). Lignite, peat or wood was heated in stages to 540°C at 10 MPa for about 10 minutes. Water was removed as liquid, and carbonization occurred. The moisture content was reduced from 30 percent to 5 percent with, however, significant loss of solid material.

A nonevaporative chemical dewatering process (henceforth abbreviated to "thermal dewatering") has been described by Evans and Siemon (1970). Australian brown coals with up to 66 percent water were heated to temperatures

up to 300°C with a saturated steam atmosphere, similar to the Fleissner process. However, the temperature was reduced before the pressure was released, to prevent "flashing" of steam. Since all the water is removed as liquid, the energy requirements are low, about 20 percent of that required in evaporative drying. Comparatively little degradation occurred. Evans and Siemon estimated that the overall cost (mine to boiler) was about 50 percent of that of conventional evaporative drying.

In Phase I of this work (Saskatchewan Power Corporation, 1979) experiments were conducted to determine if a thermal dewatering process could be developed that would be suitable for Canadian lignites. Experiments were carried out on samples from four geographic areas of Saskatchewan [Estevan, La Ronge, Shaunavon and Coronach (Wood Mountain)] and one from Ontario (Onakawana). The results indicated that the moisture content could be reduced from typically 40 percent (bed moist) to 12 percent by treatment at 300°C for 5 minutes. The heating value increased from typically 14,000 Jg^{-1} to 21,000 Jg^{-1} (wet basis) with 96 percent of the original heating value retained in the solid product.

In Phase II (Saskatchewan Power Corporation, 1980) the laboratory scale experiments were extended. Thermal dewatering in a reactive atmosphere (H_2 or H_2/CO) and thermal dewatering with the sample immersed in oil (similar to No. 2 Fuel Oil) appeared to be more effective than regular dewatering (immersion in water) at temperatures up to 250°C. From 2 percent to 9 percent of oil was adsorbed. Some preliminary dewatering experiments were also done at temperatures above 300°C.

During the current work, Phase III, these experiments were continued on lignites from Onakawana, Ontario, Estevan and Coronach, Saskatchewan, and peat from Garrick, Saskatchewan. A new autoclave was used to perform experiments at temperatures up to 400°C. Another autoclave, with high heating rates, was used for experiments with short residence times. Experiments were also done with the lignite immersed in crude oil (light and heavy oil).

Soluble impurities, especially sodium, are removed from lignite during dewatering. A variety of chemical and physical analyses were carried out to monitor the changes in properties and composition of the lignite during thermal dewatering.

2.0 DESCRIPTION OF LIGNITE AND PEAT SAMPLES

Lignites from three geographical areas of Canada (Onakawana, Ontario and Estevan and Coronach, Saskatchewan) and one peat sample (from Garrick, Saskatchewan) were used. These samples are described below while the chemical and physical analyses are given in Appendix A. All samples were stored under nitrogen at 5°C.

2.1 Lignite from Onakawana, Ontario

A 5 kg sample was obtained from Manalta Coal Limited. The sample was collected in 1979, and was stored and shipped under water in a sealed drum.

The sample was physically quite different from those used in Phase I of this work. It consisted of distinctly woody material mixed with earthy (silt-like) material. Very little peat type material was present. The Phase I sample had been a mixture of woody and peat type material.

Separation of the woody and earthy material had already occurred during shipment and storage, and it was not known whether the sample was originally a mixture of the two types of material, or whether the sample was actually a mixture of two separate samples, one woody and one earthy. Accordingly, experiments were done with two prepared samples. Sample ON-4S was the original sample, thoroughly mixed to ensure homogeneity.

The second sample, ON-4, was obtained from ON-4S by washing and sieving to >10 mesh. Sample ON-4 constituted 39 percent of ON-4S (dry basis) and had

a 10.6 percent ash content (dry basis). The <10 mesh residue, which was not thermally dewatered separately, constituted 61 percent of ON-4S (dry basis) and had an ash content of 36 percent (dry basis) and a heating value of 16,560 Jg^{-1} (wet basis).

The analytical data for ON-4, Appendix A, was similar to that obtained for other samples of Onakawana lignite (Friedrich et al., 1972; 1974).

2.2 Lignite from Estevan, Saskatchewan

Samples were collected during spring and early summer, 1980. They were obtained from freshly mined coal faces, or from previously mined coal faces by removing the first 0.5 m of coal. The following is a list of locations, dates and designations for the lignite samples.

2.2.1 Boundary Dam Mine (Manitoba and Saskatchewan Coal Company Limited)

a) Sample designation: BDM-5 Sampling date: 1980 April 18

Details: A scoop sample was taken from Pit 1, Cut 46, Station 16, at the working face. This was a 4 m thick seam with 20 m of overburden.

b) Sample designation: BDM-6 Sampling date: 1980 May 26

Details: A scoop sample was taken from Pit 1, at the east end of the working face. This end of the face is close to Long Creek and the seam was observed to be wet.

2.2.2 Bienfait Mine (Manitoba and Saskatchewan Coal Company Limited)

a) Sample designation: BM-5 Sampling date: 1980 May 26

Details: A scoop sample was taken from Pit 8, Station 84, at the working face. The seam was 3 m thick with 20 m of overburden.

2.2.3 Souris Valley Mine (Saskatchewan Power Corporation)

a) Sample designation: SV-6 Sampling date: 1980 April 18

Details: A scoop sample was taken from the working face, 400 m from the west end of the pit. This was a 4 m seam with clay partings and 6 m of overburden.

b) Sample designation: SV-7 Sampling date: 1980 April 18

Details: The sample was taken from a clarain band containing vitrain, fusain and durain bands, 1 m from the base of the 4 m seam, at the same location as SV-6.

c) Sample designation: SV-8 Sampling date: 1980 April 18

Details: A sample was collected from the north spoil wall, at the west end of the pit, from the middle of the 2.5 m seam.

d) Sample designation: SV-9 Sampling date: 1980 June 17

Details: A scoop sample was taken from the deepest part of of the working seam (east end, overburden 18 m).

e) Sample designation: SV-10 Sampling date: 1980 June

Details: A fresh representative sample was provided by Saskatchewan Power Corporation. This sample was obtained by augering from the working face.

2.2.4 Coronach Mine (Saskatchewan Power Corporation)

a) Sample designation: CM-5 Sampling date: 1980 April 25

Details: A sample was collected from the south (spoil) wall, station 2100 + 25, from the middle of the 4 m seam (16 m overburden). The sample consisted of clarain, with bands of vitrain, fusain and woody material.

b) Sample designation: CM-6 Sampling date: 1980 April 25

Details: A sample was collected from the working face, 1 m from the base of a 4 m seam with 13 m overburden. The sample consisted of clarain, with bands of vitrain, fusain and attrital matter.

c) Sample designation: CM-7 Sampling date: 1980 April 25

Details: A scoop sample was taken from the working face.

2.3 Peat

Sample designation: PM-3 Sampling date: 1978

Details: Obtained from the Saskatchewan Department of Mineral Resources (Troyer, 1978), the peat sample was collected in 1978 from Garrick, Saskatchewan (and stored in sealed drum under water at room temperature). The sample used for the experiments was taken from the middle of a 30 kg sample, and was, therefore, presumably not oxidized during storage. It was of rank H=4 to 5 on the von Post scale. (Fuchsman, 1980).

2.4 Crude Oil

a) Sample designation: Light Crude Oil (LCO)

Details: A sample of light crude oil was obtained on 1980 June 15 from Saskatchewan Oil and Gas Corportion. This oil was a Viking crude, Dodsland type 2-8-31-22. The heating value was 44,750 Jg^{-1}.

b) Sample designation: Heavy Crude Oil (HCO)

Details: A sample of heavy crude oil was also obtained from Saskachewan Oil and Gas Corporation on 1980 June 15. This was a Bakkan crude, Dodsland type 7-12-32-23-W3. The heating value of this oil was 40,960 Jg^{-1}.

3.0 EXPERIMENTAL PROCEDURES

3.1 Thermal Dewatering Experiments

3.1.1 Thermal Dewatering at Temperatures up to 310°C

The apparatus and procedure were identical to those used in Phase II of this program. A detailed description of both is given in the Phase II report.

In these experiments the sample (30 to 60 g in size) was weighed into a wire mesh basket, and immersed in 150 mL water in the autoclave (Parr 4563 Mini-Reactor). The autoclave was flushed with nitrogen, sealed, and heated to the reaction temperature. The time required to reach reaction temperature was approximately 40 minutes. After it had been held at the reaction temperature for the nominal residence time (usually 5 minutes), the sample was removed from the water by means of a specially designed lifting mechanism and the autoclave cooled. The cooling time was approximately 30 minutes.

The total mass loss of the sample was determined from its initial and final weight. Solid material which was lost through the mesh of the basket was recovered from the liquid by filtration. The amount of recovered liquid was determined by weighing. The liquid contained water soluble material (inorganic salts and organics), the total amount of which was determined by evaporating an aliquot at 30°C. The amount of gas formed was determined by PVT measurements.

The mass of water collected after the experiment was also used to determine the moisture left in the sample. This moisture content is given in Appendix B as the "moisture content, by difference in weight of water".

The subsequent analyses of the products of thermal dewatering are described in Section 3.3.

In some experiments only 40 mL of water was used in order to determine the effect of heating the sample in a steam atmosphere rather than immersed in liquid water. This amount of water was just sufficient to saturate the atmosphere in the bomb at the reaction temperature.

3.1.2 Thermal Dewatering at Temperatures Above 310°C

The maximum temperature that could be used with the Parr Model 4563 Mini-Reactor was 310°C. Experiments at temperatures higher than 310°C were done using a Parr Model 4652 reactor. This reactor could be used to 600°C and 25 MPa. The internal volume of this autoclave was similar to the Parr Model 4563 Mini-Reactor, (500 mL), and the experimental procedures were similar. The differences were:

a) The reactor was not equipped with a stirrer, so that the sample could not be removed from the water by the technique used in the low temperature experiments. Instead, at the end of the heating period the reactor was lifted from the heater (so that it could be quickly cooled) and turned upside-down, by a pulley system

operated by remote control. The samples location within the bomb was such that turning the bomb upside-down removed the sample from the liquid water.

b) The reactor was not equipped with gas valves, so that no gas samples could be directly removed for analysis. Samples were obtained for analysis from a port on the rupture disc assembly by use of a gas syringe.

c) For experiments at 400°C (which is above the critical temperature of water) the volume of the bomb was reduced to 350 mL by use of stainless steel packing.

3.2 Thermal Dewatering Experiments at Short Residence Times

The autoclave systems used in the normal experiments described in Section 3.1 had large heat resistances. Consequently it took 40 minutes or longer to heat them to the reaction temperature and a further 30 minutes to cool the contents. This meant that the sample was above the temperature at which significant reaction took place (>250°C) for much longer than the nominal residence time at which it was held at the reaction temperature. A 5 minute residence time at 300°C implied a total time of 20 minutes above 250°C.

A small autoclave was used to obtain data at short residence times. This was a Parr Model 4740 reactor, volume 70 mL, which was heated in a fluidized sand bath.

The sample (10 g) was weighed out, and held in the bottom of the

autoclave by wire mesh. (Figure 3.2.1). 15 mL of water was added which was sufficient to cover the sample. The autoclave was closed and completely submerged in the sand of the preheated fluidized sand bath. It took 11 -12 minutes to bring the autoclave to the reaction temperature (250°C to 350°C), and, for a nominal zero minute residence time at 300°C, the autoclave was above 250°C for approximately 5 minutes (heating and cooling), compared with 15 minutes for the regular experiments.

The autoclave was removed from the fluidized bath at the end of the residence time, inverted so that the sample was no longer immersed in water, and cooled.

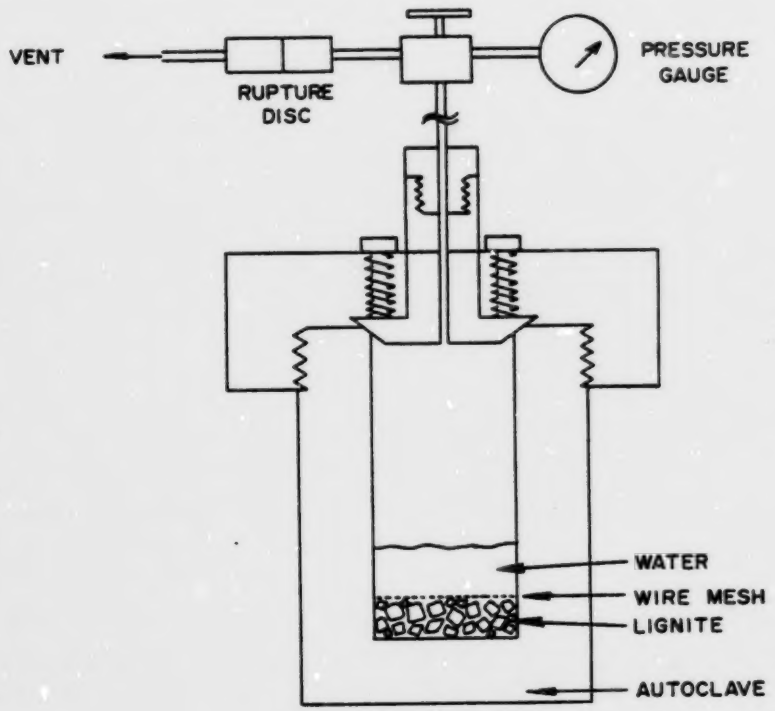


Figure 3.2.1. AUTOCLAVE FOR EXPERIMENTS WITH SHORT RESIDENCE TIMES

Only limited analytical data could be obtained from these experiments, because the amount of gas and liquid formed could not be determined. The bomb was not fitted with valves, but some gas samples were obtained by loosening the pressure gauge fitting and collecting, via a tube, the gas that "leaked" from a port of the rupture disc assembly.

3.3 Chemical and Physical Analyses

Three different sets of chemical and physical analyses as well as mass balances were determined in Phase III.

Set 1. For every experiment.

a) mass balance

b) moisture content (solid product)

c) heating value and sulphur content (solid product)

d) percent solubles (in aqueous product)

e) sodium and potassium concentration (in aqueous product).

Set 2. For a large number of selected experiments:

f) equilibrium moisture content (solid product)

g) proximate analysis (solid product)

h) pH (aqueous product)

i) chemical composition of gaseous product.

Set 3. For a limited number of samples (generally four feedstocks and products of eight experiments):

j) ultimate analysis (solid product)

k) spontaneous combustion (solid product)

l) density (solid product)

m) grindability (solid product)

n) free swelling index (solid product)

o) major and trace elements (solid product)

p) major and trace elements (aqueous product)

q) anions (aqueous product)

r) total organic and inorganic carbon (aqueous product)

s) biological oxygen demand (aqueous product).

a) Mass Balance

The amounts of solid and liquid reactants and products were determined by direct weighing (± 0.0001 g solids, ± 0.1 g liquids). The amount of gas was determined by PVT measurements. The mass balance was usually better than ± 0.5 g (in 200 g), which is the total estimated uncertainty in the weighings involved. Full details were given in the Phase II Report.

b) Moisture Content, Solid Product

Three methods were used, and the results are quoted in Appendix B.

i) ASTM D 3173-73 Method, Modification 1:

The moisture content was determined by the ASTM:D 3173-73 procedure, which involves measuring the loss in weight (assumed to be water) when a 1 g sample is heated in an oven for 1 hour at 104 - 110°C. There were two variations from this standard

procedure. The sample was contained in a 250 mL conical flask, through which dried air was passed at a flow rate of 100 mL min^{-1}. The air was dried by passing it over Drierite instead of through sulphuric acid. Tests showed that these two variations did not affect the results.

ii) ASTM D 3173-73 Method, Modification 2: The procedure outlined in i) was followed, but the amount of water evolved during heating was determined by passing the air through weighed drying tubes containing Drierite and weighing the tubes after 1 hour.

iii) Moisture by Difference in Weight of Water: The moisture content of the solid product was determined from the masses of initial sample and solid product, moisture content of initial sample, and mass of water collected (Section 3.1.1).

Methods i) and ii) gave identical ($\pm$ 0.2 percent) results for the original samples (feedstocks). The results differed by up to 5 percent for the solid products of thermal dewatering. This is because gases other than water vapour are evolved during the heating. These gases (or their precursors) are formed during the thermal dewatering process. The concentrations of the gases proved to be too low for quantitative chemical analysis.

Method iii) gave results up to 10 percent lower than those obtained by methods i) and ii), due to errors caused by incomplete recovery of solid and aqueous products.

Method ii) gives the most reliable data. The results obtained by methods i) and iii) are quoted to enable comparisons to be made with Phases I and II of this work.

c) Heating Value and Sulphur Content, Solid Product

Heating values were determined using a Parr Model 1261 isothermal-jacket bomb calorimeter, following the ASTM:D 3286-73 procedure.

The sulphur content was determined by analyses of the bomb washings obtained during the heating value determinations. The washings were titrated with barium hydroxide and sodium carbonate/hydrochloric acid to determine the amount of sulphuric acid formed (Gallenkamp, 1965; Neavel et al., 1979).

d) Percent Solubles in Aqueous Product

An aliquot of the aqueous product was evaporated to dryness at 30°C. Dissolved gases and volatile organics would be lost in this procedure, but these are not significant (Phase I and II reports).

e) Sodium and Potassium Concentration in Aqueous Product

An aliquot was analysed by atomic absorption spectroscopy (Cook, 1979).

f) Equilibrium Moisture Content, Solid Product

The ASTM:D 1412-74 procedure was used, except that the moisture content after equilibration was found using methods i) and ii) in Section 3.3 (a) above.

g) Proximate Analysis, Solid Product

i) Moisture. Section 3.3 (a)

ii) Volatile Matter. The ASTM:D 3175-77 procedure, with the modifications for sparking fuels, was followed.

iii) Ash. The dry sample from the moisture determinations was used to determine the ash content, following the ASTM:D 3174-73 procedure.

h) pH, Aqueous Product

pH was measured using a conventional pH meter.

i) Chemical Composition, Gaseous Product

The gases were analysed using a Carle Model 111-H (Application 158-B) gas chromatograph. This turnkey system (effectively six columns with a hydrogen transfer tube) analysed for H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3+C_4, CO_2, CO, H_2S, SO_2, O_2, N_2 and H_2O.

j) Ultimate Analysis, Solid Product

Monenco Analytical Laboratories, Calgary.

Analyses k) through s) are discussed in Section 8.0.

4.0 REMOVAL OF WATER DURING THERMAL DEWATERING OF LIGNITE

The amount of water removed during thermal dewatering of Canadian lignites at temperatures up to 300°C was investigated in Phases I and II of this program. In Phase III these measurements were extended to temperatures up to 400°C. Additional experiments were done with a different design of apparatus that enabled thermal dewatering experiments to be done with short residence times. These experiments are described separately.

Extensive experimentation was done on three lignites: one (ON-4) from Onakawana, Ontario; and two (BM-5 and SV-7) from Estevan, Saskatchewan. Limited experiments were also done on eight other Saskatchewan lignites, and one peat sample (described in Section 7.0). The results will be discussed in detail for each sample with a summary of data and conclusions presented in Section 9.0.

4.1 Thermal Dewatering of Onakawana Lignite

One sample of Onakawana lignite was split into two (Section 2.0) because of its high clay content. ON-4S was the original sample including the silt, ON-4 was prepared by washing to remove the silt.

Sample ON-4 was thermally dewatered at temperatures from 200°C to 400°C. The results are summarised in Table 4.1.1. The residence time at the thermal dewatering temperature is a nominal 5 minutes [in practise close to 20 minutes because of the slow heating and cooling, (Section 3.1)]. An exception is the data at 200°C, taken for a nominal residence time of 60 minutes because

thermal dewatering is slow at 200°C.

The moisture content decreases with increasing temperature. The heating value on a dry basis also increases with reaction temperature, mainly because of the decrease in the oxygen content of the solid product. (The heating value on a wet product basis reflects the changes in the moisture content and in the heating value on a dry basis.)

Table 4.1.1. THERMAL DEWATERING OF ONAKAWANA LIGNITE (ON-4)

	Equilibrium Moisture %	Heating Value, J g^{-1} Wet Basis	Dry Basis
Original Sample	41.8 (43.8)[1]	13,450	23,930
After Thermal Dewatering at:			
200°C	20.7 (36.6)	16,320	25,740
250°C	22.5 (35.3)	16,530	25,540
275°C	-- (32.3)	18,120	26,750
300°C	17.4 (28.1)	18,740	26,060
310°C	16.5 (26.4)	20,120	27,340
350°C	11.6 (30.9)	19,030	27,540
370°C	10.8 (25.0)	18,180	24,240
400°C	7.8 (25.4)[2]	20,080	26,920

[1] Numbers in brackets indicate measured percent moisture of product after dewatering.

[2] The original moisture for this sample was 49.0 percent.

The equilibrium moisture level for the original sample (41.8 percent) was similar to the actual moisture level (43.8 percent). The equilibrium moisture level for thermally dewatered lignite was much lower than the moisture level in the product, by 16 percent at 200°C and 10 percent at 310°C. This would

indicate that water was held in the pores and fissures of the dewatered lignite. This could be clearly seen at the higher temperatures, when vacuoles were formed, which often contained water. Further evidence that the samples readsorb moisture above the equilibrium value at NTP is given by the relation between the particle size and product moisture as shown in Table 4.1.2.

Table 4.1.2. EFFECT OF PARTICLE SIZE ON THERMAL DEWATERING OF ONAKAWANA LIGNITE AT 300°C

Particle Size	Moisture[1] %	Heating Value, J g^{-1} Wet Basis	Dry Basis
0.2 cm	32.2	17,810	26,270
0.5 cm	28.1	18,740	26,060
0.7 cm	27.6	18,450	25,490
2.0 cm	24.6	19,920	26,420

[1] ASTM D3173 Modification 2

Inspection of the data in this table suggests that the dewatered lignite has adsorbed water, presumably during the cooling of the sample. A similar effect was reported by Evans and Siemon (1970) in their study on dewatering of brown coals. To further test this hypothesis, the moisture contents of the lignite products from Table 4.1.2 were plotted against the lignite particle size. Figure 4.1.1 shows that the experimental data (reduced to dimensionless units, see Appendix F for details) are closely correlated by a theoretical curve for adsorption of water into a sphere, controlled by diffusion within the particle. These results are in apparent contradiction to data obtained for Estevan lignite (Section 4.2).

Sample ON-4S contained silt, and had a higher moisture content and ash content than ON-4 (moisture percent 52.6 and 43.8, ash percent 15.8 and 10.6

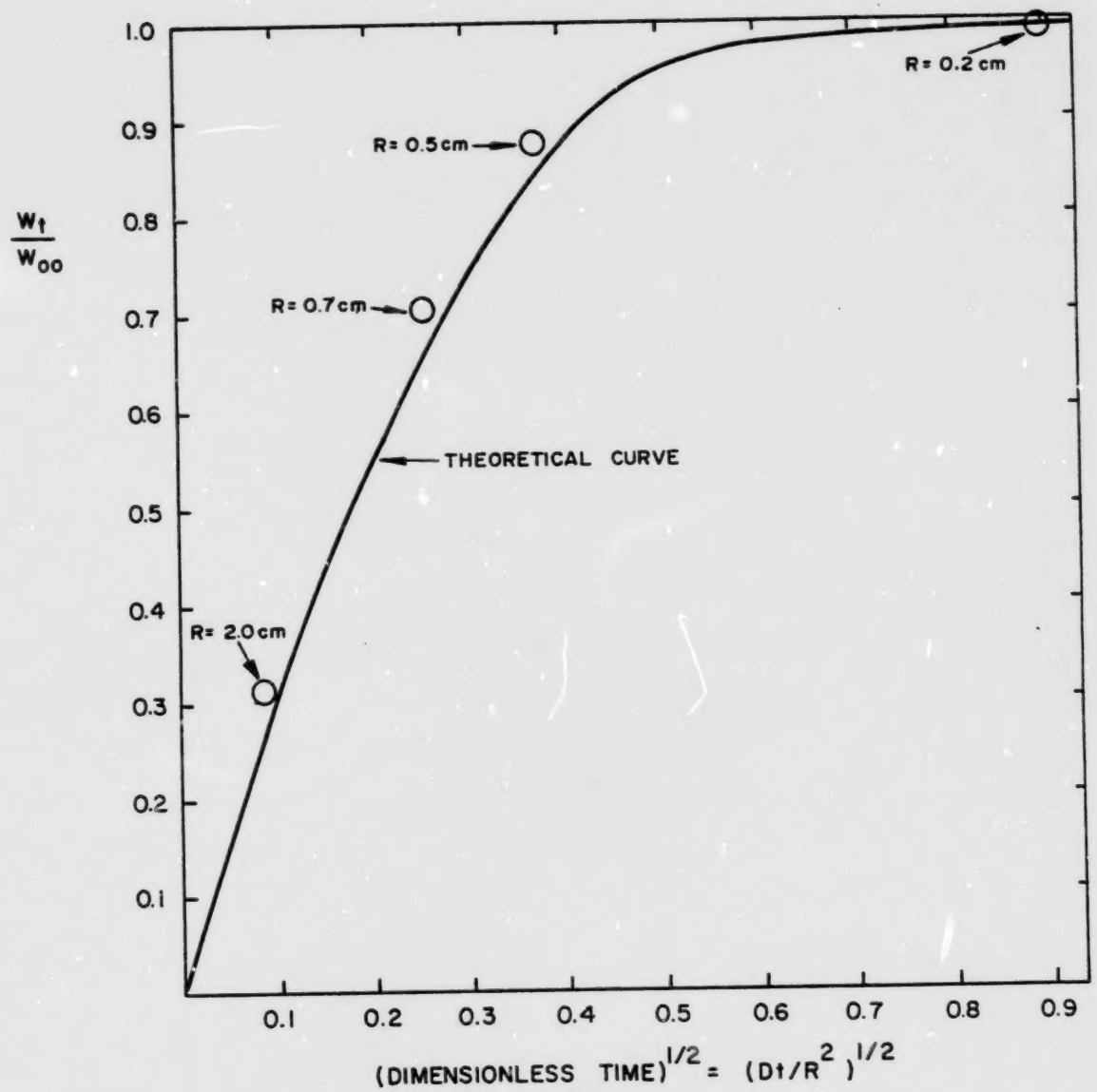


Figure 4.1.1 EXPERIMENTAL DATA AND THEORETICAL CURVE FOR ADSORPTION OF WATER BY SPHERE.

respectively) and a lower heating value. It thermally dewatered in a similar way to ON-4 (Table 4.1.4) except that the variation in the amount of silt produced large scatter in the data.

Table 4.1.3. THERMAL DEWATERING OF ONAKAWANA LIGNITE (ON-4S)

	Equilibrium Moisture, %	Heating Value, J g^{-1} Wet Basis	Dry Basis
Original Sample	27.6 (52.6)	11,110	23,420
After Thermal Dewatering at:			
250°C	18.8 (24.8)	16,130	22,520
300°C	12.7 (31.2)	15,020	21,840
310°C	-- (24.6)	17,070	22,650

4.2 Thermal Dewatering of Estevan Lignite

a) BM-5 (Bienfait Mine)

This sample was thermally dewatered at temperatures from 275°C to 400°C. The results are summarised in Table 4.2.1. The equilibrium moisture content was reduced from 31.9 percent to about 15 - 18 percent. There was an increase in the heating value (dry basis) with reaction temperature, which was also reflected in the heating value (wet basis).

b) SV-7 (Souris Valley Mine)

The results are summarised in Table 4.2.2. The equilibrium moisture content was reduced to 15.6 percent at 350°C. The regular increase in heating value (dry basis) with temperature was substantiated by a marked decrease in oxygen content (Table 4.2.3) due to evolution of H_2O and CO_2 formed by the breakdown of oxygen functional groups.

Table 4.2.1. THERMAL DEWATERING OF ESTEVAN LIGNITE (BM-5)

	Equilibrium Mositure, %	Heating Value, J g^{-1} Wet Basis	Dry Basis
Original Sample	31.9 (34.7)	16,860	25,800
After Thermal Dewatering at:			
275°C for 5 minutes	19.3 (22.8)	19,490	25,250
300°C for 5 minutes	18.0 (26.9)	20,610	26,390
350°C for 5 minutes	15.7 (20.2)	22,700	29,950
370°C for 5 minutes	18.8 (19.6)	23,040	28,660
400°C for 5 minutes	14.4 (24.2)	22.700	29,950
275°C for 60 minutes	17.3 (26.5)	20,340	27,680
350°C for 60 minutes	14.6 (19.2)	22,370	27,680
370°C for 60 minutes	19.8 (20.4)	24,210	30,420

Table 4.2.2. THERMAL DEWATERING OF ESTEVAN LIGNITE (SV-7)

	Equilibrium Mositure, %	Heating Value, J g^{-1} Wet Basis	Dry Basis
Original Sample	33.4 (36.5)	16,130	24,640
After Thermal Dewatering at:			
250°C for 5 minutes	26.1 (28.0)	18,270	25,380
275°C for 5 minutes	27.8 (32.7)	18,490	27,480
300°C for 5 minutes	20.0 (22.2)	20,400	26,220
350°C for 5 minutes	14.2 (23.0)	21,870	28,400
370°C for 5 minutes	17.1 (25.6)	19,630	26,380
400°C for 5 minutes	12.2 (26.4)	20,090	27,290
200°C for 60 minutes	22.2 (33.2)	17,715	26,520
250°C for 60 minutes	19.7 (23.8)	18,390	25,960
275°C for 60 minutes	26.2 (31.5)	19,040	27,790
350°C for 60 minutes	15.6 (26.5)	21,140	28,760
370°C for 60 minutes	17.4 (24.4)	22,120	29,260

Table 4.2.3. C, H AND O CONTENT (DRY BASIS) OF THERMALLY DEWATERED LIGNITE[1]

	C %	H %	O %
BM-5 (Estevan)			
Original Sample	64.6	5.3	19.1
After Thermally Dewatering at:			
300°C	66.7	5.5	16.5
370°C	71.3	4.6	11.7
SV-7 (Estevan)			
Original Sample	63.6	5.3	18.9
After Thermal Dewatering at:			
300°C	65.5	5.2	17.6
370°C	70.7	4.7	12.7

[1] 5 minute residence time

The effect of particle size is shown in Table 4.2.4. With both BDM-6 and SV-7 there is a definite increase in final moisture content with increase in particle size. This trend is opposite to that observed for Onakawana lignite. At present, there is no complete explanation for this apparent contradiction. A conclusion that these opposing trends are due to natural differences between Estevan lignites and Onakawana lignites is questionable, both intuitively and in light of the facts that there is no significant difference between the extent of lowering of the equilibrium moisture contents of the various samples and that, in previous studies, lignites from both areas dewatered equally well. Other possible reasons for the high final moisture contents of Estevan lignites are discussed in detail in Section 4.5.

Table 4.2.4. EFFECT OF PARTICLE SIZE ON THERMAL DEWATERING OF ESTEVAN LIGNITE AT 300°C[1]

	Moisture[2] %	Heating Value, J g^{-1} Wet Basis	Dry Basis
Sample BDM-6			
Particle Size			
0.5 cm	22.3	19,540	25,150
2.0 cm	36.5	17,930	28,240
Sample SV-7			
Particle Size			
0.5 cm	22.2	20,400	26,220
0.7 cm	27.8	19,540	27,070
2.0 cm	30.2	18,890	27,060

[1] 5 minute residence time

[2] by ASTM D3173 Modification 2

4.3 Thermal Dewatering of Coronach Lignite

The results are summarized in Table 4.3.1. The equilibrium moisture was reduced from 34 - 35 percent in the original sample to 17 - 20 percent. There was also an increase in the heating value (dry basis). The heating value on a wet basis increased from an average of 13 990 J g^{-1} (original sample) to 17 240 J g^{-1} after thermal dewatering at 300°C, or by 23 percent.

The change in the product moisture content was less marked, from an average of 37 - 40 percent in the original sample to 26 - 28 percent. The reasons for this discrepancy were discussed in Section 4.1.

Table 4.3.1. THERMAL DEWATERING OF CORONACH LIGNITE

	Eq. Moisture %	Heating Value, J g^{-1} Wet Basis	Dry Basis
CM-5			
Original Sample	34.0 (36.5)	14,140	22,270
After Thermal Dewatering at:			
250°C (5 min)	26.7 (27.0)	16,250	22,260
300°C (5 min)	20.9 (25.7)	17,660	23,770
CM-6			
Original Sample	-- (39.8)	13,950	23,180
After Thermal Dewatering at:			
300°C (5 min)	-- (28.1)	16,470	22,910
CM-7			
Original Sample	34.7 (38.9)	13,870	22,700
After Thermal Dewatering at:			
150°C (60 min)	21.1 (37.0	15,180	24,100
200°C (60 min)	20.0 (31.9)	17,150	25,180
250°C (5 min)	17.6 (24.0)	17,230	22,670
275°C (5 min)	23.4 (26.4)	18,660	25,360
275°C (60 min)	17.8 (24.9)	18,480	24,610
300°C (5 min)	17.8 (25.6)	17,600	23,650
310°C (5 min)	18.9 (21.6)	19,110	24,370
350°C (5 min)	16.1 (21.7)	19,900	25,410
370°C (5 min)	14.2 (26.6)	20,040	27,300
400°C (5 min)	11.6 (23.6)	21,120	27,650

4.4 Thermal Dewatering with Short Residence Times

The apparatus used for the preceeding thermal dewatering experiments had a large heat resistance. This meant that the rate of heating was quite low, requiring 40 minutes to heat to a typical reaction temperature of 300°C, and a similar time to cool down. Consequently, a nominal 5 minute residence time at a reaction temperature of 300°C implied a total time of 20 minutes above 250°C (the temperature at which chemical reaction of lignite becomes significant).

A system with a small heat resistance (Section 3.2) was used for some experiments. These "short residence time" experiments involved a total time of 9 minutes above 250°C for an experiment with a residence time of 5 minutes at 300°C.

Only a limited number of experiments were done with this apparatus. The sample size was small (restricting the number of analyses that could be done on the products) and it was not possible to recover all of the water for a mass balance. Experiments were done on two samples (BM-5 and SV-7) at temperatures between 250°C and 350°C, and on one sample (CM-7) at 300°C.

The results for BM-5 and SV-7 are summarized in Tables 4.4.1 and 4.4.2 respectively, together with corresponding data from the previous experiments in the higher heat resistance apparatus. The heating values of the products of thermal dewatering show a clear variation with temperature and with residence time, as would be expected. After thermal dewatering at 250°C and a 0 minute residence time (heat up and cool down only) there is very little change in heating value (24,660 Jg^{-1} versus 24,830 Jg^{-1} for the original sample, Table 4.4.1) indicating that very little reaction has occurred under

these conditions. However, after 5 minutes at this temperature, there has been a measurable increase in heating value, to 25,590 J g^{-1}.

Table 4.4.1. THERMAL DEWATERING OF ESTEVAN LIGNITE (BM-5) WITH SHORT RESIDENCE TIMES (SRT)[1]

	Eq. Moisture %	Heating Value J g^{-1} (dry basis)
Original Sample	31.9 (32.1)	24,830
After Thermally Dewatering at:		
250°C, 0 min, SRT	27.3 (26.7)	24,660
250°C, 5 min, SRT	29.5 (21.9)	25,590
275°C, 5 min	-- (22.8)	25,250
275°C, 60 min	-- (26.5)	27,680
300°C, 0 min, SRT	20.2 (20.3)	25,150
300°C, 5 min, SRT	21.7 (18.4)	26,160
300°C, 5 min	20.0 (21.9)	26,390
350°C, 0 min, SRT	16.2 (24.5)	25,590
350°C, 5 min, SRT	13.2 (15.1)	26,980
350°C, 5 min	15.7 (20.2)	29,650
350°C, 60 min	14.6 (20.4)	27,680
370°C, 5 min	18.8 (19.6)	28,660
370°C, 60 min	19.8 (20.4)	30,420

1 SRT = Short residence time in low heat resistance bomb. All other results are from larger autoclaves with long heat up and cool down times.

The equilibrium moisture contents decrease regularly with increasing temperature up to about 350°C, the rate of decrease being greater for the short residence time experiments. The final moisture content of the product does not show such a well defined trend, indicating that in these experiments the moisture content does not directly depend upon the extent of chemical reaction that has occurred. Factors such as retention and adsorption of water in fissures may also be involved here. In all three sets of short residence experiments (Table 4.4.1), a residence time of 5 minutes gives a drier product than one of 0 minutes. Longer residence times give marginally lower mositure contents.

Table 4.4.2. THERMAL DEWATERING OF ESTEVAN LIGNITE (SV-7) WITH SHORT RESIDENCE TIMES (SRT)

	Eq. Moisture %	Heating Value J g^{-1} (dry basis)
Original Sample	33.4 (34.5)	24,640
After Thermally Dewatering At:		
250°C, 0 min, SRT	31.7 (20.5)	25,120
250°C, 5 min, SRT	27.4 (25.5)	25,350
250°C, 5 min	-- (28.0)	25,380
250°C, 60 min	-- (23.8)	25,960
300°C, 0 min, SRT	32.3 (24.3)	26,070
300°C, 5 min, SRT	19.2 (22.4)	26,080
300°C, 5 min	20.0 (21.9)	26,390
350°C, 0 min, SRT	17.0 (20.0)	23,860
350°C, 5 min, SRT	16.1 (22.6)	27,540
350°C, 60 min	15.6 (19.2)	27,680

Conclusion

The moisture content does appear to vary with residence time. At temperatures of 250 - 300°C a total time of at least 10 minutes above 250°C is probably required while at temperatures above 300°C a 5 minute residence time appears to be sufficient for optimum drying.

4.5 Comparison of the Results of Thermal Dewatering Experiments in Phases I, II, and III

It is apparent from an examination of the results from Phase II of this program that the measured moisture content of the dewatered lignite samples was consistently higher than the equilibrium moisture values. The amount by which these two values differed was inconsistent and probably a function of particle size, cooling rate, drying in steam or liquid water and other factors. Only a few equilibrium moisture values were determined in Phase II.

In Phase III it was felt that a better indicator of the effectiveness of the dewatering process was the equilibrium moisture value, since this value is an inherent characteristic of the dewatered lignite and very much less dependant upon the variables stated above than is the measured moisture content. Consequently, equilibrium moisture values were measured for most of the products of thermal dewatering in the present study. It is felt that this "excess moisture" which is present over and above the equilibrium moisture can be controlled by the design of the product let-down system in future continuous processes.

Table 4.5.1 shows that while the equilibrium moisture values were comparable between Phases II and III for the various lignites, a much wider variation in final moisture contents is seen between Phase I and Phases II and III.

Table 4.5.1. COMPARISON OF THERMAL DEWATERING AT 300°C OF LIGNITES IN PHASES I, II AND III

Sample	Moisture %		
	Hot Oven Method (ASTM:D 3173)	By Water Lost During Expt	Equilibrium Moisture
Phase 1			
ON-1 (Onakawana)	12.7	8.6	--
ON-2 (Onakawana)	13.3	5.9	--
ON-3 (Onakawana)	16.9	14.0	--
BDM-3 (Estevan)	18.0	13.7	--
BM-2 (Estevan)	13.2	4.5	--
SV-3 (Estevan)	18.8	10.7	--
Phase II			
BDM-4 (Estevan)	29.4	20.0	16.6
SV-4 (Estevan)	32.6	27.5	20.9
SV-5 (Estevan)	13.2	12.3	14.7
Phase III			
ON-4 (Onakawana)	28.1	16.4	17.4
ON-4S (Onakawana)	31.2	25.7	12.7

Table 4.5.1. COMPARISON OF THERMAL DEWATERING AT 300°C OF LIGNITES IN PHASES I, II AND II (Continued)

Sample	Moisture % Hot Oven Method (ASTM:D 3173)	By Water Lost During Expt	Equilibrium Moisture
Phase III (cont.)			
BDM-5 (Estevan)	30.2	29.9	17.1
BDM-6 (310°C) (Estevan)	39.3	34.1	21.2
BM-5 (Estevan)	21.9	20.0	14.7
SV-6 (Estevan)	27.8	19.7	14.5
SV-7 (Estevan)	26.2	23.5	19.2
SV-9 (Estevan)	35.3	27.9	15.9
SV-10 (Estevan)	30.1	29.5	--

In order to determine whether these differences were due to experimental error arising from small differences in procedures between the phases, the following factors were investigated:

a) Variation in design of sample holder. Drainage from the sample holder when the sample is removed from the liquid water for cooling could effect the final moisture content since some water is readsorbed during cooling (Phase II Report). Different designs of sampler holder (varying the mesh size) had no effect on the moisture content.

b) Variation in the temperature at which the reactor pressure is released. This was nominally 25°C. Tests showed no significant change in moisture content if the temperature was as high as 50°C (maximum handling temperature). At higher temperatures considerable evaporation could be expected, as this is the basis of the Fleissner process.

c) Variation in the time between opening the reactor and analyzing the product. The sample was usually removed from the reactor, dried with paper towels to remove water droplets on the outside of the sample and, within 10 minutes, stored in sealed plastic containers. Tests were made to ascertain the amount of moisture that could be lost by evaporation at room temperature. A sample (ON-4) that had been thermally dewatered at 300°C was left exposed at 23°C and 41 percent relative humidity (ambient). The loss in weight was, after 5 minutes, 0.6 percent; 10 minutes, 1.4 percent; 50 minutes, 7 percent; 100 minutes, 11 percent; 200 minutes, 15 percent. The loss is considerable over long periods of time, but is negligible for periods of up to 10 minutes. Another sample (BDM-6), also thermally dewatered at 300°C, lost 0.8 percent in weight over 9 minutes.

d) Properties of lignite samples used for dewatering. One possible major difference between the samples used in Phases I, II and III was the extent of oxidation (weathering) of the original samples. Even slight oxidation affects the reactivity of coals other than anthracite (Berkowitz, 1979). While care was taken to minimize oxidation of the samples during storage, possible oxidation of the coal in situ, before collection, was not investigated at that time.

Petrographic analysis can determine the degree of oxidation of coal. Petrographic analyses of some of the samples were performed by the Energy Research Unit, University of Regina. These analyses were not part of the present work, so that the choice of sample appears arbitrary, but they were made on samples collected at the same time and location as the samples used for thermal dewatering.

Figure 4.5.1 shows some photographs (x250, oil immersion) of lignites used during Phases II and III. Numbers 1 - 3 are of Estevan lignite (SV-7) and show well developed microfissures in vitrinite. This is considered to be a positive indication of oxidation (weathering) (Chandra, 1962), and the sample would be classified as oxidized. Numbers 4 - 6 (Estevan lignite, BM-5) have very well developed microfissures indicating that this sample is severely oxidized, while 7 - 8 indicate that Estevan lignite BDM-5 is not very oxidized. These lignites (Table 4.5.2) did not yield a dry product upon thermally dewatering.

Photographs number 9 - 11 are of Onakawana lignite (ON-4) which appears fresh and unoxidized. This sample did give a dry product when thermally dewatered. Numbers 12 - 13 (Coronach lignite, CM-5) do not show any microfissures, but the sample is high in inerts, and also has a high mineral content within the macerals, both factors that could reduce its reactivity and account for its high final moisture content.

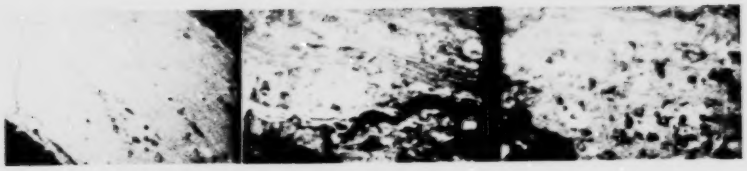
Figure 4.5.2 shows photographs (x250, oil immersion) of lignites used in Phase I. None of the samples show microfissures, and all thermally dewatered successfully (Table 4.5.2).

Oxidation could occur during the preparation of samples for petrographic analyses. However, the samples in Figures 4.5.1 and 4.5.2 were prepared and mounted by the same operator using basically similar techniques, so that this would not appear to be a factor in this case.

A possible explanation for this difference in weathering is that the samples, especially those from Estevan used during Phase I were collected

1 2 3 4 5

6 7 8 9 10

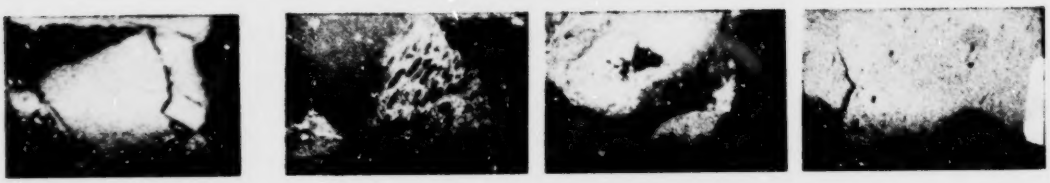


11 12 13

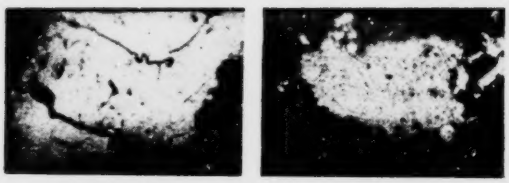
Numbers:
1 - 3 Estevan Lignite (SV-7)
4 - 6 Estevan Lignite (BM-5)
7 - 8 Estevan Lignite (BDM-5)
9 - 11 Onakawana Lignite (ON-4)
12 - 13 Coronach Lignite (CM-5)

Figure 4.5.1. PHOTOGRAPHS (X 250, OIL IMMERSION) OF LIGNITE SAMPLES USED DURING PHASES II AND III

3 4 5 6 7



8 9 10 11

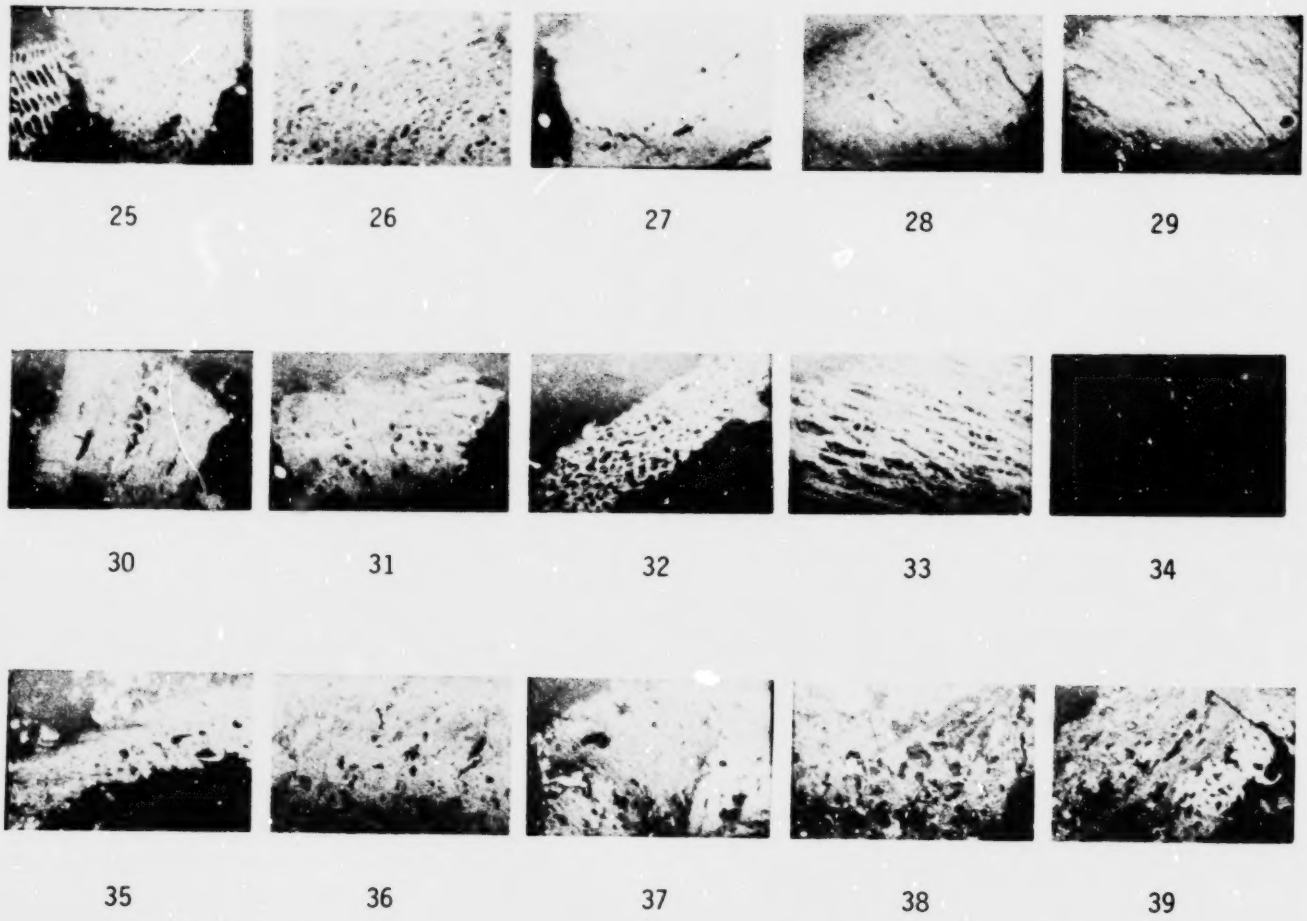


23 24

Numbers: 3 - 11 Coronach Lignite (CM-1, CM-2, CM-3)

23 - 24 Estevan Lignite (KM-2)

Figure 4.5.2. PHOTOGRAPHS (X 250, OIL IMMERSION) OF LIGNITE SAMPLES USED DURING PHASE I



Numbers: 25 - 33 Estevan Lignite (KM-3)

34 - 36 Estevan Lignite (BDM-3)

37 - 39 Estevan Lignite (BM-2)

Figure 4.5.2. (Continued)

Table 4.5.2. COMPARISON OF EXTENT OF OXIDATION OF ORIGINAL SAMPLES (DETERMINED BY PETROGRAPHIC ANALYSES) AND MOISTURE CONTENT OF PRODUCTS OF THERMAL DEWATERING AT 300°C

Sample	Extent of Oxidation	Moisture %
BM-2	None	13.2
SM-2	None	14.5
CM-3	None	16.9
ON-4	None	28.1
BDM-5	Slight Oxidation	27.5
SV-7	Well Oxidized	22.2
BM-5	Severely Oxidized	21.9
CM-5	Mineralization, High Inerts	25.7

during a wet spring, after a couple of wet years. The seams were moist, with much liquid water present. The samples for Phase III were collected after a couple of dry years. Since the overburden is removed 1 - 2 months before the lignite is mined, weathering of the relatively dry lignite, sufficient to affect its reactivity, could occur. The mine engineers at both the Souris Valley and the Boundary Dam mines confirmed our observations, and commented that in 1978 the seams in both mines were very wet, with the water table probably in the coal seam. Since then both mines have been getting progressively drier, due to climatic change, and mining of shallower seams.

Fresh samples were collected from the Souris Valley Mine when a newly opened face close to the lake was being worked. The seam was very wet, possibly because of seepage from the lake. The samples, SV-9 and SV-10, did not give lower measured moisture contents after thermal dewatering than SV-7.

4.6 Statistical Treatment of the Results of Thermal Dewatering Experiments in Phase III

Variations in lignite characteristics, temperature and time of dewatering, and experimental set-up used all contribute to the difficulties in assessing the extent of dewatering and in predicting the nominal moisture content in products from a commercial dewatering plant. At the same time, a general quantitative description of the product moisture and its dependence on process variables is required for design purposes and for process evaluation. The data from the Phase III dewatering experiments were, therefore, subjected to Multiple Linear Regression Analysis, in order to generate a design equation which would facilitate the analysis of costs and technical feasibility of the process.

Since, as discussed previously, the equilibrium moisture content is felt to be the most meaningful measure of the change in lignite characteristics on dewatering, the equation was derived in terms of the equilibrium moisture contents of the products expressed as a percentage of the equilibrium moisture content of the feedstocks. The actual moisture content can probably be controlled at a level above or below the equilibrium moisture value by design of the product removal and let-down system. These reduced moisture values were correlated with time and temperature, resulting in the following regression equation:

$$\% \text{ of Initial Equilibrium Moisture Remaining} = 112 - 0.19\,(\text{Temperature, °C}) - 0.11\,(\text{Time, min})$$

This equation is valid only over the temperature range studied. The standard

deviations and coefficients for the regression equation are given in Table 4.6.1.

Table 4.6.1 RESULTS OF REGRESSION ANALYSIS ON PHASE III DEWATERING DATA

	Coefficient	Std. Error	F	R^2
Temperature	-0.192	0.035	29.529	0.41 (Simple)
Time	-0.113	0.083	1.831	0.03 (Simple)
Regression Equation	--	10.8	15.68	0.41 (Multiple)
Constant	112.0	--	--	--

Figure 4.6.1 presents the regression line calculated for a retention time of 5 minutes. The experimental data for 5 and 60 minutes as well as the 90 percent confidence intervals are included, as are some data points reported in the literature for research studies and operating plants. It should be noted that the data from literature refer to actual moisture contents rather than equilibrium moistures. Plants operating on the Fleissner principle involve flash evaporation of 20 to 30 percent of the lignite moisture resulting in decreased final moisture contents.

It can be concluded that the derived linear equation provides a conservative measure of the extent of dewatering in the temperature range 250 - 370°C for retention times of 5 to 60 minutes.

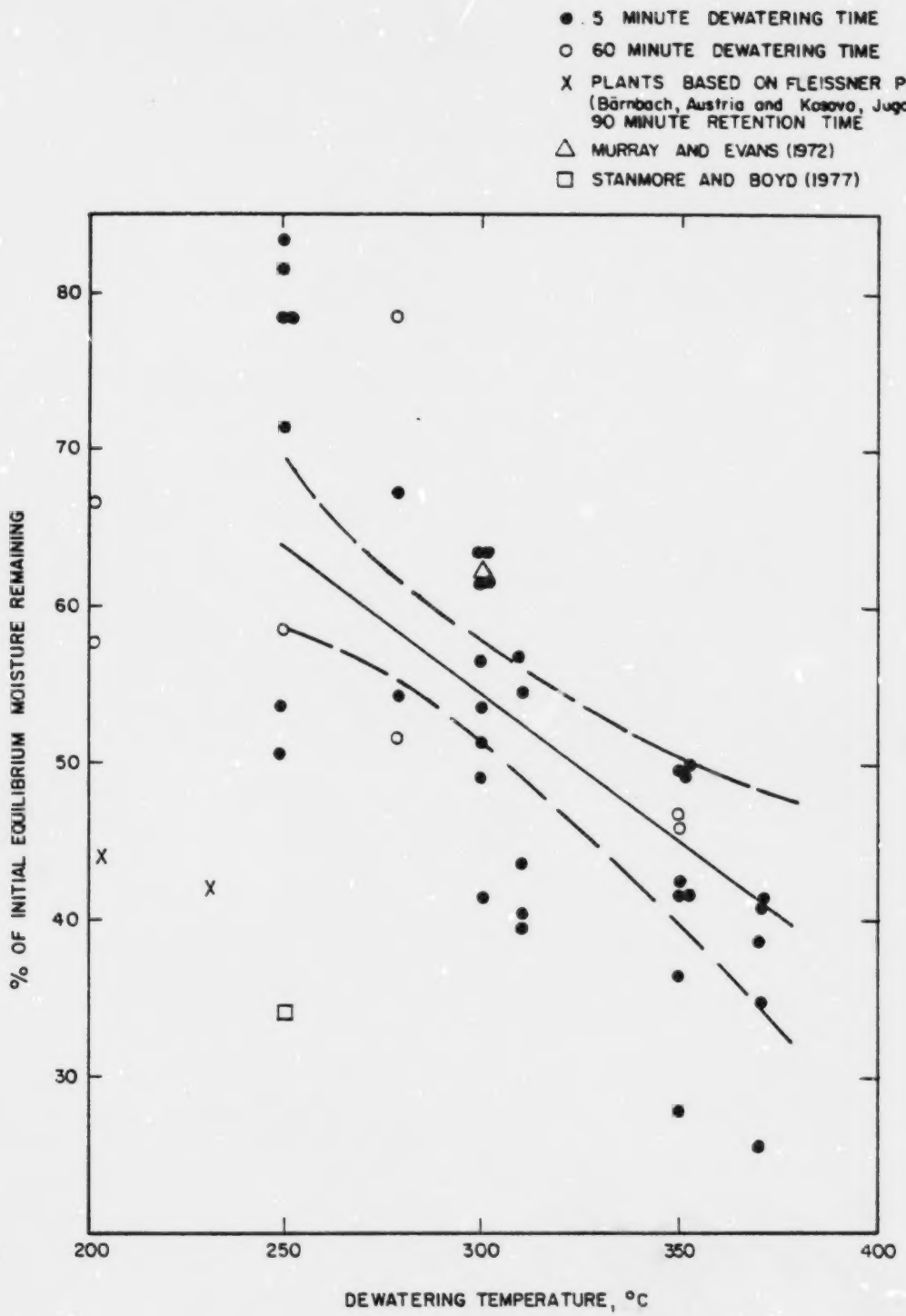


FIGURE 4.6.1 REGRESSION LINE FOR 5 MINUTE RETENTION TIME

5.0 REMOVAL OF SODIUM AND OTHER WATER SOLUBLE MATERIAL DURING THERMAL DEWATERING

When lignite is thermally dewatered it is in contact with hot liquid water. This results in the removal of nearly all of the water soluble material that is present. Tests were carried out to determine the extent and selectivity of removal of these soluble materials during dewatering.

5.1 Total Amount of Water Soluble Material Removed During Thermal Dewatering

The total amount of water soluble material removed during thermal dewatering was determined for each experiment (Section 3.3). The results are given in Appendix B. This material consisted of inorganic salts (mainly sodium chloride and sodium sulphate) and also organic compounds produced by the thermal degradation of the lignite. These materials are discussed separately in later sections of this chapter.

The amount of water soluble material removed depended upon the sample (Table 5.1.1). The data in Table 5.1.1 include results obtained from Phase I and II experiments. There is a large variation, even within the samples from the same seam. This is a result of differences in the inorganic and maceral composition within the coal seam. The amount of inorganic salts often varies with the location of the sample.

Table 5.1.1. VARIATION OF THE AMOUNT OF WATER SOLUBLE MATERIAL EXTRACTED WITH SAMPLE, FOR THERMAL DEWATERING AT 300°C[1]

	% Mass of Water Soluble Material Removed (based on dry weight of lignite)	
	Range	Mean
Onakawana Lignite (3 samples)	1.5 to 2.5	1.8
Estevan Lignite:		
Bienfait Mine (2 samples)	2.0 to 2.7	2.4
Boundary Dam Mine (4 samples)	2.0 to 4.1	3.0
Klimax Mine (1 sample)	--	1.0
Souris Valley Mine (7 samples)	1.5 to 5.2	3.3
Coronach Lignite (6 samples)	0.9 to 4.0	2.6
Shaunavon Lignite (3 samples)	0.3 to 1.3	0.9

[1] Including data from Phases I and II

The amount of water soluble material removed also varied with the temperature (Table 5.1.2). (Data was not obtained at temperatures above 300°C because of experimental difficulties in recovering all of the water, and separating the water from the coal oil that was formed.)

Table 5.1.2. EFFECT OF TEMPERATURE ON THE AMOUNT OF WATER SOLUBLE MATERIAL EXTRACTED DURING THERMAL DEWATERING

	% Mass of Water Soluble Material Removed (based on dry weight of lignite)
Estevan Lignite (SV-7) Dewatered at:	
200°C	1.4
250°C	1.8
275°C	2.6
300°C	4.6

The effect of temperature on the removal of water soluble material was significant for the Estevan lignites and Coronach lignites, the amount of dissolved material increasing three-fold in going from 200°C to 300°C. The effect was small for the Onakawana lignites.

5.2 Removal of Sodium During Thermal Dewatering

The variation in sodium content of lignites from various deposits is demonstrated by the fact that, in general, lignites from Onakawana and Coronach contain low amounts of sodium (less than 1 percent Na in ash) while Estevan lignite contains much larger amounts of sodium (from 3 percent to 8 percent Na in ash).

Sodium is removed during thermal dewatering in two ways. Free sodium salts are dissolved in the hot water as are the salts formed when decarboxylation of the lignite releases sodium that was bound as $-COO^-Na^+$. Some

sodium is present as siliceous material, and is not removed.

The concentration of sodium in the aqueous product of thermal dewatering was measured by an atomic absorption (AA) technique (Section 3.3). The results are given in Appendix C. This data, together with the total amount of aqueous product formed, gave the amount of sodium removed during thermal dewatering. Subtraction from the amount of sodium present in the original sample (Section 3.3 and Appendix C) gave the sodium content of the solid product. Although the amount of sodium present was not determined for all original samples, the sodium removed has been calculated from the AA data for the aqueous products.

As a check on the above procedure, the ashes of some of the products and feedstocks were analyzed directly for sodium by AA (atomic absorption) and by ICP-AES (inductively coupled plasma-atomic emission spectroscopy). The data (Table 5.2.1) shows good agreement between the aqueous phase method and the ash analysis method. Both these methods give generally lower results than the ICP-AES method. However, all these methods verify the decrease in sodium content during thermal dewatering.

The results are given as the sodium content of the lignite (dry lignite basis), and not as the sodium content of the ash, because a proximate analysis (percent ash) was only done for selected products. The sodium content (ash basis) is given, when it could be calculated, in parentheses in the remainder of this section.

Table 5.2.1. COMPARISON OF THE SODIUM CONTENTS OF THE SOLID PRODUCTS OF THERMAL DEWATERING[1]
Sodium, ppm (dry lignite basis)

	Ash Analyses Method	Aqueous Phase Method	ICP[2] AES
Onakawana Lignite (ON-4)			
Original Sample	890	--	1,500
Dewatered at 300°C	220	220	440
Estevan Lignite (BM-5)			
Original Sample	3,100	--	4,200
Dewatered at 300°C	3,000	2,100	3,500
Estevan Lignite (SV-7)			
Original Sample	6,800		6,700
Dewatered at 300°C	5,600	5,500	4,200

[1] Obtained by direct ash analysis, and from the composition of original sample and amount of sodium present in the aqueous product.

[2] Inductively coupled plasma-atomic emission spectroscopy.

The data for all experiments is given in Appendix B. Table 5.2.2 gives the sodium content for some products of thermally dewatered Estevan lignite (SV-7) after dewatering at various temperatures.

Table 5.2.2. SODIUM CONTENT OF THERMALLY DEWATERED ESTEVAN LIGNITE (SV-7)

	Sodium, ppm (dry lignite basis)
Original Sample	6,800 (ash 6.4%)
Washed Samples	6,630
After Thermally Dewatering at:	
250°C for 5 minutes	5,480 (ash, 6.4%)
275°C for 5 minutes	5,910
300°C for 5 minutes	4,530 (ash 4.0%)
200°C for 60 minutes	5,960 (ash 6.9%)
250°C for 60 minutes	4,880 (ash 4.9%)
275°C for 60 minutes	5,170
350°C for 60 minutes	3,990
370°C for 60 minutes (100 mL water)	4,510 (ash 4.3%)
300°C for 5 minutes (40 mL water)	5,380
300°C for 5 minutes, 0.7 cm lumps	5,070
300°C for 5 minutes, 2 cm lumps	5,520
250°C, short residence time	5,300
300°C, short residence time	5,400
350°C, short residence time	5,700

The original sample contained 6,800 ppm sodium (dry basis) or 6.4 percent sodium in the ash. A control test was run to determine whether some of this sodium could be removed by simple washing with water. This was determined by stirring the sample (0.5 cm lumps) in hot (60°C) water for one hour. The lignite/water ratio was 1/5 on a weight basis. This treatment removed very little sodium, reducing the sodium content from 6,800 ppm to 6,630 ppm. The

final concentration of sodium in the wash water was low, about 20 ppm. Fowkes (1978) reported contrary results when he removed 10 -20 percent of the sodium originally present in North Dakota lignite by exhaustive extraction with distilled water. This discrepancy may be due to a difference in particle size between the experiments. Paulson (1979), found, for example, that the ion migration rate within the particles was the controlling factor in removing sodium by ion exchange.

Thermal dewatering significantly reduced the sodium content. Very little chemical reaction (indicated primarily by the evolution of gas, or by changes in the properties of the lignite) occurred with sample SV-7 at temperatures below 300°C. Consequently the reduction in sodium content from 6,800 ppm to 5,500 ppm (mean of data at 300°C to 275°C) is a result of solution of salts present in the coal gel.

Chemical reaction of organic sodium salts (carboxylates) becomes significant at 300°C and is parallelled by a reduction in sodium content to 4300 ppm (mean for data at 300°C and above). Based on evolved CO_2 in gaseous products, if every CO_2 molecule formed freed a sodium atom the sodium content would decrease by 10,000 ppm, not the observed additional reduction of 5,500 - 4,300 = 1,200 ppm. The remainder of the carboxylate groups were probably protonated or coordinated to metals other than sodium.

All of the above data refers to experiments in which lignite (30 to 50 g) is immersed in 150 mL of water during the thermal dewatering process. Some experiments were done with only 40 mL of water present (Table 5.2.2), where the only liquid water that is in contact with the lignite is the water that is evolved by the lignite as it dries. At 300°C, with 40 mL of water, the sodium

content of SV-7 was reduced to 5,380 ppm (from 6,630, as washed feed was used for these experiments). This result indicates that a high proportion of the removed sodium leaves the lignite dissolved in the removed water.

The lignite was also not immersed in liquid water in the short residence time experiments (Table 5.2.2). While the amount of sodium removed almost doubled as the temperature was increased from 250°C to 350°C, the concomitant decrease in mass resulted in an increase in sodium content of the product.

The lignite from the Bienfait Mine in Estevan (BM-5) had a lower sodium content than SV-7, but the removal of sodium was similar at the same thermal dewatering conditions (Table 5.2.3). Table 5.2.4 shows the data for Onakawana lignite (ON-4). The data for the other samples are in Appendix B.

Table 5.2.3 SODIUM CONTENT OF THERMALLY DEWATERED ESTEVAN LIGNITE (BM-5)

	Sodium, ppm (dry lignite basis)[1]
Original Sample	3,100
Washed Sample	2,930
After Thermally Dewatering at:	
275°C for 5 minutes	2,030
300°C for 5 minutes	1,480
370°C for 5 minutes	935
250°C, short residence time	2,300
300°C, short residence time	2,300
350°C, short residence time	2,500

[1] By ICP-AES

Table 5.2.4. SODIUM CONTENT OF THERMALLY DEWATERED ONAKAWANA LIGNITE (ON-4)

	Sodium, ppm (dry lignite basis)
Original Sample	890
Washed Sample	635
After Thermally Dewatering at:	
250°C for 5 minutes	335
275°C for 5 minutes	287
300°C for 5 minutes	192
310°C for 5 minutes	174
200°C for 60 minutes	327
275°C for 60 minutes	312
310°C for 5 minutes (40 mL water)	282
300°C for 5 minutes (2 cm lumps)	221

Conclusions

The amount of sodium removed from the lignites increased significantly with temperature. Washing with warm (60°C) water decreased the sodium content by about 5 - 20 percent depending on the lignite (the sodium in sample ON-4 was significantly decreased by simple washing). Thermal dewatering at temperatures below 275°C reduced the sodium content by 20 - 35 percent while dewatering at 300°C and above decreased the sodium content by 35 - 80 percent. There does not appear to be any advantage in sodium removal in going to long residence times.

This large decrease in sodium content could significantly affect the combustion properties of the lignites with respect to slagging and fouling.

The net effect of removal of various metal ions on the fouling tendencies of these lignites will be discussed in the following section.

5.3 Removal of Potassium and Calcium During Thermal Dewatering

The removal of potassium during thermal dewatering was also determined by ash analysis of the original samples and by analysis of the potassium in the aqueous products. The technique was similarly checked by analysing the ash of selected products (Table 5.3.1). The agreement between the two methods is not good. This was mainly because the concentration of potassium in the aqueous product was low (5 ppm to 30 ppm) and consequently susceptible to errors due to adsorption of potassium on any solids (e.g. clay) present. These factors were not investigated because the amount of potassium present and removed is negligible compared with sodium.

Table 5.3.1. POTASSIUM CONTENT OF THE SOLID PRODUCTS OF THERMAL DEWATERING[1]

	Potassium, ppm (dry lignite basis)		
	Ash Analysis	Aqueous Phase Analysis	ICP-AES
Onakawana Lignite (ON-4)			
Original Sample	440	--	280
Dewatered at 300°C	110	340	130
Estevan Lignite (BM-5)			
Original Sample	530	--	190
Dewatered at 300°C	350	490	150

Table 5.3.1. POTASSIUM CONTENT OF THE SOLID PRODUCTS OF THERMAL DEWATERING[1] (continued)

	Potassium, ppm (dry lignite basis)		
	Ash Analysis	Aqueous Phase Analysis	ICP-AES
Estevan Lignite (SV-7)			
Original Sample	780	--	270
Dewatered at 300°C	350	780	500

[1] Obtained by direct ash analysis, and from the composition of the original sample and amount of potassium present in the aqueous product.

Table 5.3.2 gives the potassium content of thermally dewatered Estevan lignite (SV-7). Potassium is removed during thermal dewatering, but the accompanying decrease in dry weight results in no significant net change in the potassium as percentage on a dry product basis. Similar results were obtained for the other lignites investigated.

Table 5.3.2. POTASSIUM CONTENT OF THERMALLY DEWATERED ESTEVAN LIGNITE (SV-7)

	Potassium, ppm (dry lignite basis)
Original Sample	780
After Thermally Dewatering at:	
250°C for 5 minutes	760
275°C for 5 minutes	780
300°C for 5 minutes	740
200°C for 60 minutes	780
250°C for 60 minutes	740
275°C for 60 minutes	730
370°C for 60 minutes (100 mL water)	710

Calcium was also removed during thermal dewatering. The concentration of calcium in the aqueous product was determined for a few samples by atomic absorption (Appendix B). The concentration of calcium in the original sample, solid product and aqueous product was also determined by ICP-AES for a few selected samples (Appendix C and D).

The slagging and fouling of boilers occurring during combustion of lignite has been shown to increase with increasing sodium content and to decrease with increasing calcium and magnesium content (Anderson et al., 1977). Markley (1967) put forth a "Dolomite Ratio" as an indicator of the slagging tendency of an ash. An increase in the Dolomite ratio indicates a decreased tendency for an ash to cause slagging problems.

$$\text{Dolomite Ratio} = \frac{\%CaO + \%MgO}{\%CaO + \%MgO + \%K_2O + \%Na_2O + \%Fe_2O_3}$$

Table 5.3.3 shows some representative ratios for feedstocks and products. These have been calculated from the ICP-AES measurements (Appendix C) of the concentrations of these metals. In each case, the ratio is seen to increase with increasing severity of dewatering conditions, an indication that thermally dewatered lignite might be expected to cause less slagging and fouling problems during combustion.

Another measure of the relative tendency of a coal to foul heat transfer surfaces is the Fouling Index (Allardice, 1978) as given below:

$$\text{Fouling Index} = 0.064\ Si + 0.132\ Fe + 0.085\ Ca + 0.438\ Mg + 0.570\ Na - 0.106$$

where Si, Fe, etc. represent the percent of each element on a dry coal basis.

This relationship was developed for Australian brown coals, but the relative values should be valid for lignites as well. The calculated values of Fouling Index (Table 5.3.3) follow the same pattern as the Dolomite Ratio (a decrease in Fouling Index indicates that less fouling should occur).

Table 5.3.3. EFFECT OF THERMAL DEWATERING ON THE DOLOMITE RATIO AND FOULING INDEX OF LIGNITES[1]

Sample (Experimental Conditions)	Dolomite Ratio	Fouling Index
ON-4 (original sample)	0.44	0.27
ON-4 (300°C)	0.68	0.16
BM-5 (original sample)	0.71	0.45
BM-5 (300°C)	0.73	0.43
BM-5 (370°C)	0.79	0.47
SV-7 (original sample)	0.57	0.52
SV-7 (300°C)	0.63	0.40
SV-7 (370°C)	0.70	0.40

[1] Indicators of slagging and fouling characteristics during combustion.

6.0 THERMAL DEWATERING UNDER CRUDE OIL

In Phases I and II some experiments were done in which lignite was thermally dewatered while immersed in oil. Two types of oil were used, light cycle oil, a by-product from the catalytic cracking of crude oil and similar to No. 2 Fuel Oil, and slurry oil, which is similar to No. 6 Fuel Oil (Bunker C). Slurry oil showed little advantage over water, but light cycle oil was definitely superior, especially at temperatures of 300°C and less.

In the current work two crude oils provided by Sask Oil were used. One was a heavy crude oil, the other a light crude oil, both from Dodsland, (Lloydminster).

The experimental procedure was similar to that used for thermal dewatering under water (Section 3.1) except that the samples were immersed in 150 mL of oil instead of 150 mL of water. A small amount (30 - 40 mL) of water was added to the oil. This was to ensure that the atmosphere inside the reactor was saturated with water vapour at the reaction temperature, and that, consequently, no water was removed from the sample by evaporation.

A total of 12 experiments were done on 4 different samples. The results for sample SV-7 (Estevan lignite) are summarized in Table 6.1. The use of light crude oil resulted in a product moisture content (15 percent) which was 7 percent lower than that obtained using water alone. The equilibrium moisture content was also lower, 20 percent with water alone and 15 percent with light crude oil. These reductions, however, are not large enough to offset the cost of the light oil, of which 10 percent (dry basis) was adsorbed by the lignite.

Thermal dewatering was very effective when the sample was immersed in heavy crude oil. The final moisture content averaged 6 percent, compared to 22 percent with water alone. The equilibrium moisture contents were 11 percent with heavy crude oil, and 20 percent with water alone. About 2 percent (dry basis) of the heavy oil was adsorbed by the lignite.

An experiment was done with heavy crude oil that had been used in a previous thermal dewatering experiment (recycled heavy crude oil). Thermal dewatering was not enhanced, and the moisture content (26 percent) of the product was similar to that obtained using water alone (22 percent).

Two experiments were done with heavy crude oil and 110 ml of water, 70 ml in excess of that required to saturate the bomb with water vapour. With heavy crude oil and excess water (present as liquid) the moisture content of the dewatered lignite was 25 percent.

Table 6.1. YIELD, MOISTURE CONTENT AND HEATING VALUE OF THE SOLID PRODUCT OF THERMAL DEWATERING OF SAMPLE SV-7 IN CRUDE OIL AT 300°C

Conditions	Yield Mass %	Moisture[1] %	Heating Value J g^{-1} (dry basis)
Water only	78	22.2	26,220
Light Crude Oil	76	15.3	31,620
Heavy Crude Oil	76	6.4	28,890
Recycled Heavy Crude Oil	--	25.7	28,730
Heavy Crude Oil (excess water)	82	24.6	27,310
Recycled Heavy Crude Oil (excess water)	--	27.0	28,430

[1] ASTM D3173 Modification 2

These experiments showed that, while thermal dewatering in heavy crude oil produced a product with a low moisture content and a low equilibrium moisture content, a process for lignite/oil dewatering is unlikely to be economical because dry crude oil would have to be used. The oil can not be recycled since excess water would be present and poor dewatering would result. Also, oil losses would be high.

The results for the other samples are shown in Table 6.2. The moisture contents, and equilibrium moisture contents (Appendix B) are reduced with fresh crude oil. Experiments with recycled oil or an excess of water were not done with these samples.

Table 6.2. YIELD, MOISTURE CONTENT AND HEATING VALUE OF THE SOLID PRODUCT OF THERMAL DEWATERING OF LIGNITES IN CRUDE OIL AT 300°C

Conditions	Yield Mass %	Moisture %	Heating Value J g^{-1} (dry basis)
Onakawana Lignite			
ON-4, water only	63.2	28.1	26,060
ON-4, light crude oil[1]	69.1	21[2]	30,610
ON-4, heavy crude oil	65.9	8.5	31,530
ON-4S, water only[1]	56.5	24.6	22,650
ON-4S, light crude oil[1]	79.8	17.0	26,790
Coronach Lignite			
CM-7, water only	70.3	25.6	3,650
CM-7, light crude oil	72.7	21.5	26,490
CM-7, heavy crude oil	74.6	15.8	28,160
Estevan Lignite			
BM-5, water only	78.7	18.0	26,390
BM-5, light crude oil	68.1	9.0	--
BM-5, heavy crude oil	73.7	9.4	--

[1] at 310°C

[2] by difference in weight of water

7.0 THERMAL DEWATERING OF PEAT

Some experiments on the thermal dewatering of peat at temperatures from 150°C to 300°C were done in Phase I. The peat (PM-1) that was used (the only fresh bed-moist sample available) was fibric, of rank about H = 2 on the von Post index, resembling horticultural peat when dry. This type of peat is generally considered to be too low rank for use as a fuel. The results, however, were promising. At 300°C, 78 percent of the original moisture was removed, reducing the moisture content from 83 percent to 53 percent, and increasing the heating value from 2850 to 8100 J g^{-1}.

A peat sample of rank H = 4 to 5 (PM-3) was used for the current work. This is about the highest rank of peat obtainable in Saskatchewan (Troyer, 1978) and is comparable in rank to peats used elsewhere as fuel. Sample PM-3 was thermally dewatered at five temperatures, from 250°C to 400°C. The regular procedures used for lignite were followed except that as fine particles of peat were lost from the sample basket during thermal dewatering, the mass balances for the process could not be directly determined.

The moisture contents and heating values for the products of the current and Phase I experiments are shown in Table 7.1. Significant dewatering began to occur with sample PM-1 (rank H = 2) at 250°C, and with sample PM-3 at temperatures above 300°C. The moisture contents are, however, of doubtful accuracy because large amounts of water were present as liquid in the product. This could have been removed by mechanical compression, but this was not done, since it would have introduced other variables. The results obtained for the

experiment at 350°C show a substantially lower moisture content than achieved in the other experiments. This was due to less liquid water present in the sample.

Table 7.1. MOISTURE CONTENTS AND HEATING VALUES OF THERMALLY DEWATERED PEAT

	Eq. Moisture %	Heating Value J g^{-1} (wet basis)[2]
Original Sample (PM-1)	-(83.2)[1]	2,850
After Thermally Dewatering at:		
150°C for 60 min	-(81.5)	3,790
200°C for 60 min	-(77.8)	4,900
250°C for 5 min	-(65.0)	5,830
300°C for 5 min	-(52.8)	8,110
Original Sample (PM-3)	72(83)	3,850
After Thermally Dewatering at:		
250°C for 5 min	20(78.6)	5,790
300°C for 5 min	35(80.8)	5,500
350°C for 5 min	29.2(34.8)	17,770
370°C for 5 min	10.7(61.5)	11,230
370°C for 60 min	11.7(62.5)	11,490
400°C for 5 min	5.7(54.2)	14,400

[1] Numbers in brackets represent percent moisture content as measured after dewatering.

[2] Based on moisture content after dewatering.

The equilibrium moisture contents are substantially changed by thermal dewatering, from a value of 72 percent for the original sample to 20 - 30 percent by treatment at 250° to 300°C, to 12 percent by treatment at 370°C. A

combination of thermal dewatering at 250° to 300°C, followed by mechanical drying, could produce a product with a moisture content of 30 percent (heating value 20,000 J g^{-1}) which would be stable in storage. It would be resistant to readsorption of water and, since the heat evolved by readsorption of water is one of the main causes of spontaneous ignition (Sondreal et al., 1974) it would be less likely to ignite spontaneously during storage.

8.0 MISCELLANEOUS PHYSICAL AND CHEMICAL ANALYSES

A number of physical and chemical analyses of selected initial samples and solid and aqueous products were performed. Some procedures are described in Section 3.3, the remainder below. All of the results are given in Appendices C and D. Only a few of these analyses are discussed in this section.

8.1 Trace Element Analyses

These were done by the Saskatchewan Research Council, by ICP-AES. Table 8.1.1 presents some of the results for two separate samples of the aqueous phase from thermal dewatering of sample BM-5 at 300°C, and also for replicate samples of the aqueous phase from thermal dewatering of peat, PM-3, at 370°C. The reproducibility is generally acceptable, and shows that the data is probably accurate to better than an order of magnitude. Two factors may contribute to decreased accuracy. The solutions are complex, and there will be interferences between elements that could only be eliminated by detailed analysis. Also the solutions are not homogenous, because of the presence of colloidal material.

Table 8.1.1. SELECTED TRACE ELEMENT ANALYSES[1] OF THE AQUEOUS PRODUCT OF THERMAL DEWATERING

Element	BM-5 Sample 1 (ppm)[2]	BM-5 Sample 2 (ppm)[2]	PM-3 Replicates 1 (ppm)[2]	PM-3 Replicates 2 (ppm)[2]
B	15	7	17	11
Ba	0.4	0.2	1.0	0.6
Ca	5.5	1.5	280	200
K	5	<5	10	5
Mg	2	<1	<1	<1
Na	150	200	110	81
Si	13	13	53	38

[1] Measured by ICP-AES

[2] ppm in aqueous product

Table 8.1.2 compares the analyses for sodium and potassium in the aqueous phase obtained by ICP-AES and by AA. The agreement is good, confirming that the change in sodium content of lignite during thermal dewatering, which is calculated from the sodium content of the aqueous product, is reliable.

Table 8.1.2. COMPARISON OF THE ICP-AES AND AA ANALYSES FOR SODIUM AND POTASSIUM IN THE AQUEOUS PRODUCT OF THERMAL DEWATERING

Sample (Expt'l Conditions)	Na, ppm ICP-AES	Na, ppm AA	K, ppm ICP-AES	K, ppm AA
BM-5 (300°C)	175	211	5	7
BM-5 (370°C)	680	680	25	26
SV-7 (300°C)	280	335	15	6
SV-7 (370°C)	1,100	1,000	15	30
ON-4 (300°C)	62	--	5	--
PM-3 (370°C)	95	110	7.5	10

The trace element analyses for the feedstock, solid product and aqueous product can be used, with the mass loss data from Appendix B, to calculate mass balances for each element. Selected data is shown in Table 8.1.3. The mass balances, excepting the ON-4 data, average 90 percent. This is

Table 8.1.3. MASS BALANCES FOR SELECTED TRACE ELEMENTS

Sample (Expt'l Conditions)	Mass Balance, percent Ca	K	Mg	Na	Si
ON-4 (300°C)	58	40	171(?)	44	77
BM-5 (300°C)	84	75	88	85	76
BM-5 (370°C)	90	99	93	94	420(?)
SV-7 (300°C)	92	174(?)	82	80	117
SV-7 (370°C)	101	79	93	83	218(?)

acceptable considering the uncertainties in all the data involved. Some data, marked (?) in Table 8.1.3 is suspect because of apparent poor ICP-AES data. The consistently low mass balances for ON-4 are not readily explained, but could be because a non-representative sample was submitted for analysis by ICP-AES. Table 8.1.3 does indicate, however, that the ICP-AES data is reliable to an order of magnitude, or better. This is as good as can be expected for a commercial analysis of a complex sample such as coal.

8.2 Spontaneous Combustion

Lignites sometimes spontaneously ignite when stored in large stockpiles. This is triggered by an initial self-heating, which depends upon many factors,

such as rank, particle size, storage conditions, etc. (Leonard, 1979). One important factor is the exothermic adsorption of water (Berkowitz et al., 1951). The heat produced by adsorption can be sufficient to raise the temperature of the lignite high enough that oxidation becomes significant, and ignition occurs (Sondreal et al., 1974).

Heat will only be produced by water chemically or physically adsorbing onto the coal. The amount of water that can be adsorbed would depend to a first approximation upon the difference between the actual moisture content of the lignite and its equilibrium moisture level. Thermal dewatering significantly lowers the equilibrium moisture level, and should decrease the possibility of (dried) lignite spontaneously igniting by readsorption of water.

There are no direct laboratory tests for spontaneous combustion, since it is controlled by many factors, and as defined, only occurs in large stockpiles. Computer simulation has been investigated (Sondreal et al., 1974; Nordon, 1979), but was not applicable in this case.

Two laboratory scale tests have been applied. The rate and extent of readsorption of water by thermally dewatered lignite was investigated in Phase II. A second test was investigated here. Moist oxygen, at a flow rate of 100 mL min^{-1}, was passed through 20 g of sample contained in a Dewar placed in an oven at 76°C. The temperature of the sample was monitored, to $\pm$ 0.1°C, and time/temperature plots made. Comparison of these plots for an inert sample and a lignite sample would eliminate the temperature changes due to

heat exchange (warming of the sample after it is placed in the oven) and show any temperature effect due to reaction with the moist oxygen, which could be used as a measure of the tendency for spontaneous ignition. Since no self-heating temperature effect was detected for any sample, the experiments were not extended. The approach is, in principle, sound but requires extensive development.

8.3 Density, Solid Product

Bulk density (Karr, 1978) was determined by pouring the sample (aproximately 20 g, size distribution "as is") into a container of known volume with diameter at least eight times bigger than the diameter of the largest particle. The top surface was leveled off, and the container weighed.

The data, Appendix C, is comparable to the "cubic foot weight", as determined by ASTM:D 291, except that it was determined on a smaller sample. There was a small (<10 percent) decrease in bulk density upon thermal dewatering in most cases. The data for the original samples is comparable with literature values (Friedrich, 1972). Approximate specific gravity, true specific gravity and porosity were determined following the ASTM:D 1967 procedure for coke. The apparent specific gravity was, however, obtained for 30 g samples, contained in a mesh basket. The true specific gravity was obtained for 2 g samples, using a Weld pycnometer.

The results are given in Appendix C. The uncertainties are high because there were large variations of specific gravity within the samples - portions of the samples floated on water. Flotation was probably due to air entrapped within the sample, so the floating particles were removed. In addition lignite (original sample and product) adsorbs water when immersed in liquid water. Measurements were taken after 15 minutes immersion, and would not be strictly applicable to the true sample.

The porosities were evaluated following the ASTM:D 167 procedure, and are given in Appendix C. The porosity decreases on drying for BM-5 and SV-7, as expected (Karr, 1979), because of the shrinkage of the coal gel. The porosity increases for ON-4, as expected because the product of thermal dewatering had a visibly more porous structure than the original sample. There is a high uncertainty in porosities measured by this indirect method, but a porosimeter was not available.

8.4 Grindability

The grindability was measured by the Hardgrove Machine Method (ASTM:D 409) by Commercial Testing and Engineering Co., Vancouver. The results are given in Appendix C. There is an increase in the Hardgrove Grindability Index (HGI) upon thermal dewatering, which would indicate an increase in the capacity of a coal crusher. The data for the feedstocks appear low compared with literature values. Tibbets (1978) quotes values of HGI = 55 for Estevan lignites. These results could, however, be affected by the measurement conditions, as the present samples were tested "as received", while the usual practice is to air dry the sample before measurement of grindability. Wet

samples would "ball" and would appear not to crush easily. Wet lignite samples exhibit plasticity on shearing, and give anomolous HGI results (Evans, 1978). The dewatered lignites behaved similar to higher rank coals in these tests.

8.5 Free Swelling Index

The Free Swelling Index was measured by Commercial Testing and Engineering Co., Vancouver, and is given in Appendix C. The measured index was zero for all samples, indicating that those samples had no caking properties.

8.6 Anions, Aqueous Products

The concentrations of some of the major anions in the aqueous products were determined by the Monenco Analytical Laboratories, Calgary. The results are given in Appendix D. The duplicate data for BM-5 (300°C) shows good reproducibility, except for $[S^{=}]$. Sulphide is readily oxidised, and this might have occurred in storage and transit in this case because of the variety of compounds present.

8.7 Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC), Aqueous Products

TIC and TOC was measured by Monenco Analytical Laboratories, Calgary, and the results are given in Appendix D.

8.8 Biological Oxygen Demand (BOD), Aqueous Products

BOD was measured by Monenco Analytical Laboratories, Calgary, and the data is given in Appendix D. The very large oxygen demand for the aqueous product of thermal dewatering at 370°C arises because coal liquefaction is significant at that temperature, and coal oil is present in the water.

8.9 Oxidation - Reduction Potential (ORP), Aqueous Products

ORP was measured following the ASTM:D 498 - 76 procedure. The results are given in Appendix D.

9.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 Conclusions

Thermal dewatering substantially reduces the moisture content of lignite, from bed moist values of 30 to 45 percent down to 15 to 25 percent by treatment at 300°C. The extent of drying depends upon four factors:

1. Thermal dewatering temperature. Increasing temperatures yields a drier product, but involves substantially higher pressures, since the operating pressure must be equal to or greater than the saturated vapour pressure of water at that temperature. Very little thermal dewatering occurs below 250°C, and above 350°C thermal decomposition becomes significant.

2. Residence time. A residence time of several minutes is required, but residence times longer than about 5 minutes do not yield a substantially drier product in most cases.

3. Particle size. Increasing particle size appears to decrease the product moisture content for Estevan lignites. The opposite trend was observed for Onakawana lignites.

4. Composition of the original sample. This appears to have a substantial effect. The maceral composition has some effect (especially the amount of inertinite). More significant is the extent of oxidation and mineralization of the sample.

The equilibrium moisture level of lignite is reduced by thermal dewatering, and is generally below the actual moisture level, as discussed in Sections 4.1 and 4.5. Very little readsorption of water should occur under

normal atmospheric conditions, reducing the chance of spontaneous combustion.

Mineral matter is leached from the lignite during the thermal dewatering process. Large amounts of sodium are removed, increasing the "Dolomite Ratio" which is an inverse measure of the extent of slagging and fouling to be expected during combustion.

9.2 Recommendations

Future work should include:

1. An assessment of the cost of building and operating a thermal dewatering plant. This should include an evaluation of the reduction in moisture content required to make the process economical under various use conditions.

2. An investigation into processes such as crushing or briquetting after thermal dewatering, or flashing at the end of the process, with the purpose of reducing the final moisture content as close to the equilibrium moisture content as possible.

3. An investigation of the variation of the extent of thermal dewatering with extent of oxidation or with chemical reactivity of the lignite.

4. Continuing lab scale studies to provide additional data as required for the engineering and economic studies mentioned in 1. above.

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APPENDIX A

Analytical Data for Original Samples

Sample	ON-4	BM-5	SV-7	CM-7
Source	Onakawana	Estevan	Estevan	Coronach
Equil. Moisture, %	41.8	31.9	33.4	34.7
Moisture Content, %	46.5	34.7	34.5	38.9
Analytical Data, Dry Basis				
Proximate Analysis, %				
Ash[1]	10.6	9.0	9.7	12.4
Volatile Matter	38.9	42.8	40.7	40.8
Fixed Carbon	50.6	48.2	49.6	46.8
Heating Value, J g^{-1}	23,930	25,800	24,640	22,700
Bulk Density, g mL^{-1}	0.51	0.65	0.68	0.64
Sulfur, % Dry Basis	0.40	0.44	0.37	0.65

[1]Determined In-House

Sample	ON-4S	BDM-5	BDM-6	SV-6
Source	Onakawana	Estevan	Estevan	Estevan
Equil. Moisture, %	27.6	31.0	37.2	--
Moisture Content, %	52.6	36.5	38.8	28.4
Heating Value (Dry Basis), Jg^{-1}	23,420	23,350	26,950	19,380
Sulfur (Dry Basis), %	0.40	0.20	0.20	0.30
Ash (Dry Basis), %	15.8	18.0	8.40	--
Volatile Matter (Dry Basis)	42.2	--	40.9	--

Sample	SV-9	SV-10	CM-5	CM-6
Source	Estevan	Estevan	Coronach	Coronach
Equil. Moisture, %	33.0	--	34.0	--
Moisture Content, %	36.9	34.2	36.5	39.8
Heating Value (Dry Basis), Jg^{-1}	23,120	23,950	22,270	23,180
Sulfur (Dry Basis), %	0.30	0.23	0.25	0.23
Ash (Dry Basis), %	14.3	15.6	16.9	14.2
Volatile Matter (Dry Basis)	--	--	--	--

Sample	PM-3 (Peat)
Source	Garrick
Equil. Moisture, %	72.0
Moisture Content, %	83.0
Heating Value (Dry Basis), Jg^{-1}	22,620
Sulfur (Dry Basis), %	0.16
Ash (Dry Basis), %	4.0
Volatile Matter (Dry Basis)	--

APPENDIX B

Thermal Dewatering Results for Lignites and Peat

Experiment No.	100	101	102	103
Sample	ON-4	ON-4	ON-4	ON-4
Conditions				
Sample Weight, g	25.85	26.24	27.31	25.15
Temperature, °C	200	250	250	275
Residence Time, min.	60	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	18.8	22.8	--	26.9
As Water Solubles	1.3	1.3	--	1.4
As Gas	0.9	0.9	--	1.4
Total	21.0	25.0	--	29.7
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	31.7	27.9	--	24.0
ii) ASTM:D 3173				
a) Modification 1	36.3	35.1	35.0	31.3
b) Modification 2	36.6	35.3	35.2	32.3
iii) Equilibrium Moisture	20.7	--	22.5	--
Heating Value, J g^{-1}, dry basis	25,740	25,540	--	26,750
Sulfur, %, dry basis	0.63	0.56	--	--
Sodium, ppm, dry basis	327	335	--	287
Potassium, ppm, dry basis	363	344	--	349
Liquids				
pH	5.9	6.0	6.0	5.8
% Solubles	0.5	0.1	--	0.1
Na, ppm	56	57	--	57
K, ppm	8	9	--	8
Ca, ppm	--	--	--	
Gases				
Composition, mole %			0	
CO			100	
CO_2				

Experiment No. (cont.)	104	105	106	107
Sample	ON-4	ON-4	ON-4	ON-4
Conditions				
Sample Weight, g	23.94	24.9	25.1	26.7
Temperature, °C	275	300	300	300
Residence Time, min.	60	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	34.7	33.6	33.7	33.0
As Water Solubles	1.5	1.4	1.4	1.3
As Gas	2.1	1.8	2.2	2.0
Total	38.2	36.8	37.3	36.4
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	14.7	16.2	16.1	16.9
ii) ASTM:D 3173				
a) Modification 1	28.2	28.4	28.2	31.2
b) Modification 2	28.7	24.3	27.9	32.0
iii) Equilibrium Moisture	--	17.4	--	--
Heating Value, J g^{-1}, dry basis	27,410	24,920	26,400	26,860
Sulfur, %, dry basis	0.08	1.4	0.17	0.37
Sodium, ppm, dry basis	312	192	128	248
Potassium, ppm, dry basis	339	334	334	416
Liquids				
pH	5.4	5.2	5.2	5.6
% Solubles	0.3	0.2	0.2	0.3
Na, ppm	56	58	64	66
K, ppm	10	9	9	13
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	108	109	110	111
Sample	ON-4	ON-4	ON-4	ON-4
Conditions				
Sample Weight, g	26.22	27.65	20.63	23.84
Temperature, °C	300	300	300	300
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions		10-20 mesh	0.5 cm lumps	2 cm lumps
Mass Loss, %				
As Water	--	35.5	33.3	34.6
As Water Solubles	--	2.9	1.5	1.5
As Gas	--	1.8	2.2	1.9
Total	--	40.2	37.0	38.0
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	--	19.7	25.1	14.8
ii) ASTM:D 3173				
a) Modification 1	33.5	31.8	29.8	28.0
b) Modification 2	34.1	32.2	27.6	24.6
iii) Equilibrium Moisture	--	--	--	--
Heating Value, J g^{-1}, dry basis	--	26,270	25,490	26,420
Sulfur, %, dry basis	--	0.84	--	--
Sodium, ppm, dry basis	--		92	221
Potassium, ppm, dry basis	--	470	280	343
Liquids				
pH	5.5	--	--	5.6
% Solubles	--	0.3	0.2	0.2
Na, ppm	--	82	60	53
K, ppm	--	6	12	8
Ca, ppm	--	--	--	
Gases				
Composition, mole %				
CO		0		
CO_2		100		

Experiment No. (cont.)	112	113	114	115
Sample	ON-4	ON-4	ON-4	ON-4
Conditions				
Sample Weight, g	25.37	24.50	22.85	22.16
Temperature, °C	310	310	310	310
Residence Time, min.	5	5	0	30
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	35.1	37.9	35.0	38.5
As Water Solubles	1.5	1.6	1.2	2.2
As Gas	1.3	2.0	1.6	2.8
Total	37.9	41.5	37.8	43.5
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	14.0	10.10	14.2	9.4
ii) ASTM:D 3173				
a) Modification 1	30.0	--	--	12.8
b) Modification 2	26.4	--	--	12.8
iii) Equilibrium Moisture	16.5	--	--	--
Heating Value, J g^{-1}, dry basis	27,340	28,180	--	--
Sulfur, %, dry basis	0.81	--	--	--
Sodium, ppm, dry basis	174	175	206	164
Potassium, ppm, dry basis	383	338	346	326
Liquids				
pH	5.25	5.1	5.3	5.2
% Solubles	0.3	0.2	0.2	0.3
Na, ppm	71	63	58	65
K, ppm	11	9	8	9
Ca, ppm	--	--	19	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	116	117	118	119
Sample	ON-4	ON-4	ON-4	ON-4
Conditions				
Sample Weight, g	25.68	29.8	30.22	23.8
Temperature, °C	310	310	310	310
Residence Time, min.	30	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/40	H_2O/40	H_2O/40
Special Conditions	Slow Heating	Washed Feed	Washed Feed	Sat. Sol.
Mass Loss, %				
As Water	39.9	38.8	39.9	32.6
As Water Solubles	2.1	0.7	0.7	1.0
As Gas	2.9	2.0	1.9	1.5
Total	44.9	41.5	42.5	35.1
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	7.1	37.4	27.6	17.3
ii) ASTM:D 3173				
a) Modification 1	13.8	--	29.9	30.3
b) Modification 2	15.6	--	30.1	30.7
iii) Equilibrium Moisture	18.2	16.9	16.9	--
Heating Value, J g^{-1}, dry basis	23,120	--	--	--
Sulfur, %, dry basis	--	--	--	--
Sodium, ppm, dry basis	104	325	283	--
Potassium, ppm, dry basis	298	--	--	--
Liquids				
pH	5.1	5.1	--	--
% Solubles	0.3	0.4	0.4	22.4
Na, ppm	72	95	96	71,000
K, ppm	13	21	19	51,000
Ca, ppm	45	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	120	121	122
Sample	ON-4	ON-4	ON-4
Conditions			
Sample Weight, g	8.37	7.46	7.70
Temperature, °C	350	370	400
Residence Time, min.	5	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/180	H_2O/250
Special Conditions	--	--	--
Mass Loss, %			
As Water	--	--	--
As Water Solubles	--	--	--
As Gas	--	--	--
Total	40.0	46.9	45.7
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	--	--
ii) ASTM:D 3173			
a) Modification 1	29.9	23.9	25.2
b) Modification 2	30.9	25.0	25.6
iii) Equilibrium Moisture	11.6	10.8	7.8
Heating Value, J g^{-1}, dry basis	27,540	24,240	26,920
Sulfur, %, dry basis	0.1	--	1.0
Sodium, ppm, dry basis	--	--	--
Potassium, ppm, dry basis	--	--	--
Liquids			
pH			
% Solubles			
Na, ppm			
K, ppm			
Ca, ppm			
Gases			
Composition, mole %			
CO			
CO_2			

Experiment No. (cont.)	123	124
Sample	ON-4	CN-4
Conditions		
Sample Weight, g		24.7
Temperature, °C	310	300
Residence Time, min.	5	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	oil:H_2O/100:30	oil:H_2O/100:40
Special Conditions	Light Crude	Heavy Crude
Mass Loss, %		
As Water	27.5	30.3
As Water Solubles	1.7	1.3
As Gas	1.8	2.5
Total	30.9	34.1
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	21.2	20.5
ii) ASTM:D 3173		
a) Modification 1		9.8
b) Modification 2		8.5
iii) Equilibrium Moisture	7.1	9.3
Heating Value, J g^{-1}, dry basis	30,610	31,530
Sulfur, %, dry basis	0.29	0.34
Sodium, ppm, dry basis	--	0
Potassium, ppm, dry basis	--	329
Liquids		
pH	--	
% Solubles	0.6	0.2
Na, ppm		270
K, ppm		24
Ca, ppm		
Gases		
Composition, mole %		
CO		
CO_2		

Experiment No. (cont.)	125	126	127	128
Sample	ON-4S	ON-4S	ON-4S	ON-4S
Conditions				
Sample Weight, g	39.33	45.89	40.26	38.34
Temperature, °C	250	300	310	310
Residence Time, min.	5	5	0	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	27.9	36.9	37.6	41.2
As Water Solubles	0.5	0.9	0.9	1.1
As Gas	0.9	1.3	1.6	1.2
Total	29.3	39.1	40.1	43.5
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	34.8	25.7	25.1	20.0
ii) ASTM:D 3173				
a) Modification 1	35.2	36.4	37.5	33.0
b) Modification 2	28.4	31.2	28.0	24.6
iii) Equilibrium Moisture	18.8	12.7	--	
Heating Value, J g^{-1}, dry basis	22,520	21,840	21,350	22,650
Sulfur, %, dry basis	1.6	0.99	1.1	1.0
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	--	--	6.4	6.5
% Solubles	0.1	0.2	0.2	0.3
Na, ppm	84	120	113	100
K, ppm	12	38	35	31
Ca, ppm	31	760	760	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	129	130
Sample	ON-4S	ON-4S
Conditions		
Sample Weight, g	40.75	38.02
Temperature, °C	310	310
Residence Time, min.	30	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	oil:water/120:30
Special Conditions		light crude
Mass Loss, %		
As Water	42.2	17.9
As Water Solubles	1.4	1.1
As Gas	2.4	1.2
Total	46.0	20.2
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	19.2	43.5
ii) ASTM:D 3173		
a) Modification 1	30.2	25.9
b) Modification 2	23.0	17.0
iii) Equilibrium Moisture	--	--
Heating Value, J g^{-1}, dry basis	22,230	26,790
Sulfur, %, dry basis	0.26	0.35
Sodium, ppm, dry basis		
Potassium, ppm, dry basis		
Liquids		
pH	6.2	--
% Solubles	0.3	0.3
Na, ppm	110	--
K, ppm	39	--
Ca, ppm	--	--
Gases		
Composition, mole %		
CO		
CO_2		

Experiment No. (cont.)	131	132	133
Sample	BDM-5	BDM-5	BDM-5
Conditions			
Sample Weight, g	29.68	31.11	30.03
Temperature, °C	300	310	310
Residence Time, min.	5	5	30
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions			
Mass Loss, %			
As Water	11.2	13.0	13.9
As Water Solubles	2.6	2.3	3.1
As Gas	1.4	1.9	2.5
Total	15.2	17.1	19.6
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	29.9	28.4	28.2
ii) ASTM:D 3173			
a) Modification 1	30.2	30.0	29.2
b) Modification 2	27.5	27.3	29.1
iii) Equilibrium Moisture	17.1		
Heating Value, J g^{-1}, dry basis	24,380	25,470	24,650
Sulfur, %, dry basis	0.18	0.12	0.08
Sodium, ppm, dry basis			
Potassium, ppm, dry basis			
Liquids			
pH	7.2	--	--
% Solubles	0.5	0.5	0.6
Na, ppm	420	310	400
K, ppm	7	23	9
Ca, ppm	--		
Gases			
Composition, mole %			
CO			
CO_2			

Experiment No. (cont.)	134	135	136
Sample	BDM-5	BDM-5	BDM-5
Conditions			
Sample Weight, g	7.85	7.54	7.86
Temperature, °C	350	370	400
Residence Time, min.	5	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/180	H_2O/250
Special Conditions			
Mass Loss, %			
As Water	--	--	--
As Water Solubles	--	--	--
As Gas	--	--	--
Total	29.9	31.2	40.9
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	--	--
ii) ASTM:D 3173			
a) Modification 1	22.6	21.9	20.4
b) Modification 2	23.0	17.9	21.8
iii) Equilibrium Moisture	13.3	12.3	9.0
Heating Value, J g^{-1}, dry basis	26,220	26,620	26,750
Sulfur, %, dry basis	0.1	0.1	--
Sodium, ppm, dry basis			
Potassium, ppm, dry basis			
Liquids			
pH	--	--	--
% Solubles	--	--	--
Na, ppm	--	--	--
K, ppm	--	--	--
Ca, ppm			
Gases			
Composition, mole %			
CO			
CO_2			

Experiment No. (cont.)	137	138	139
Sample	BDM-6	BDM-6	BDM-6
Conditions			
Sample Weight, g	27.71	26.67	26.78
Temperature, °C	250	300	300
Residence Time, min.	5	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions		0.5 cm lumps	2 cm lumps
Mass Loss, %			
As Water	15.7	11.0	8.0
As Water Solubles	1.1	1.8	1.5
As Gas	0.3	1.5	1.3
Total	17.1	14.4	10.8
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	27.9	32.4	34.5
ii) ASTM:D 3173			
a) Modification 1	28.7	28.4	37.0
b) Modification 2	27.4	22.3	36.5
iii) Equilibrium Moisture	26.5	--	--
Heating Value, J g^{-1}, dry basis	26,310	25,150	28,240
Sulfur, %, dry basis	0.22	0.23	0.14
Sodium, ppm, dry basis			
Potassium, ppm, dry basis			
Liquids			
pH	7.7	6.9	6.7
% Solubles	0.2	0.3	0.3
Na, ppm	99	180	125
K, ppm	4	6	7
Ca, ppm	--	--	--
Gases			
Composition, mole %			
CO			
CO_2			

Experiment No. (cont.)	140	141	142	143
Sample	BDM-6	BDM-6	BDM-6	BDM-6
Conditions				
Sample Weight, g	30.15	7.74	8.30	7.75
Temperature, °C	310	350	370	400
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/180	H_2O/250
Special Conditions				
Mass Loss, %				
As Water	8.3	--	--	--
As Water Solubles	1.7	--	--	--
As Gas	0.7	--	--	--
Total	10.7	27.6	30.2	36.9
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	34.1	--	--	--
ii) ASTM:D 3173				
a) Modification 1	39.3	21.7	24.8	20.3
b) Modification 2	38.7	22.4	25.7	21.0
iii) Equilibrium Moisture	21.2	13.5	13.0	11.1
Heating Value, J g^{-1}, dry basis	27,740	27,970	26,100	25,480
Sulfur, %, dry basis	0.05	0.2	0.4	0.2
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	7.2	--	--	--
% Solubles	0.3	--	--	--
Na, ppm	150	--	--	--
K, ppm	7	--	--	--
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	144	145	146	147
Sample	BM-5	BM-5	BM-5	BM-5
Conditions				
Sample Weight, g	28.12	27.19	26.14	34.97
Temperature, °C	275	275	300	300
Residence Time, min.	5	60	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	13.1	20.0	19.0	17.5
As Water Solubles	0.9	1.6	1.2	1.3
As Gas	0.8	0.4	1.4	1.5
Total	14.8	21.0	21.6	20.3
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	25.3	21.7	19.9	21.5
ii) ASTM:D 3173				
a) Modification 1	27.1	24.5	22.8	23.3
b) Modification 2	22.8	26.5	23.8	22.7
iii) Equilibrium Moisture	17.3		18.0	--
Heating Value, J g^{-1}, dry basis	25,250	27,680	26,950	26,310
Sulfur, %, dry basis	0.25	0.26	0.33	0.28
Sodium, ppm, dry basis	2,030	--	1,560	1,390
Potassium, ppm, dry basis	480	--	520	500
Liquids				
pH	6.6	6.7	6.9	6.8
% Solubles	0.2	0.3	0.2	0.3
Na, ppm	125	--	185	260
K, ppm	6	--	6	8
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	148	149	150	151
Sample	BM-5	BM-5	BM-5	BM-5
Conditions				
Sample Weight, g	33.19	35.74	31.79	33.10
Temperature, °C	300	300	300	300
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/40 Washed Sample	H_2O/40 Washed Sample
Special Conditions				
Mass Loss, %				
As Water	18.9	20.6	23.7	24.0
As Water Solubles	1.3	1.3	0.9	0.8
As Gas	1.5	1.5	1.3	1.4
Total	21.7	23.4	25.9	26.2
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	20.0	18.4	20.6	26.3
ii) ASTM:D 3173				
a) Modification 1	21.5	22.7	--	19.5
b) Modification 2	19.0	21.9	--	19.6
iii) Equilibrium Moisture	--	--	--	--
Heating Value, J g^{-1}, dry basis	25,720	26,560	26,800	--
Sulfur, %, dry basis	0.30	0.20	0.22	--
Sodium, ppm, dry basis	2,150	1,470	2,020	2,230
Potassium, ppm, dry basis	490	520	490	540
Liquids				
pH	6.8	6.8	--	--
% Solubles	0.3	0.3	0.6	0.5
Na, ppm	140	260	385	410
K, ppm	7	8	15	16
Ca, ppm	--	--		
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	152	153	154
Sample	BM-5	BM-5	BM-5
Conditions			
Sample Weight, g	7.12	--	51.1
Temperature, °C	350	350	370
Residence Time, min.	5	60	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions	--		Cooled in H_2O
Mass Loss, %			
As Water	--	--	--
As Water Solubles	--	--	--
As Gas	--	--	--
Total	34.8	--	35.2
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	--	--
ii) ASTM:D 3173			
a) Modification 1	20.0	19.3	19.8
b) Modification 2	20.2	19.2	19.6
iii) Equilibrium Moisture	15.7	14.6	18.8
Heating Value, J g^{-1}, dry basis	29,650	27,680	28,660
Sulfur, %, dry basis	0.3	--	--
Sodium, ppm, dry basis	--	1,600	--
Potassium, ppm, dry basis	--	--	
Liquids			
pH	--	--	--
% Solubles	--	--	--
Na, ppm	--	--	--
K, ppm	--	--	--
Ca, ppm	--	--	--
Gases			
Composition, mole %			
CO		0.7	0
CO_2		92.5	100
C_{1+}		6.0	0

Experiment No. (cont.)	155	156	157
Sample	BM-5	BM-5	BM-5
Conditions			
Sample Weight, g	7.43	56.2	6.78
Temperature, °C	370	370	400
Residence Time, min.	5	60	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions			
Mass Loss, %			
As Water	--	--	--
As Water Solubles	--	--	--
As Gas	--	--	--
Total	37.7	--	40.6
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	--	--
ii) ASTM:D 3173			
a) Modification 1	19.5	20.9	23.6
b) Modification 2	21.0	20.4	24.2
iii) Equilibrium Moisture	17.1	19.8	14.4
Heating Value, J g^{-1}, dry basis	30,000	30,420	29,950
Sulfur, %, dry basis	0.1	--	0.10
Sodium, ppm, dry basis	--	240	--
Potassium, ppm, dry basis	--	510	--
Liquids			
pH	--	--	--
% Solubles	--	--	--
Na, ppm	--	680	--
K, ppm	--	25	--
Ca, ppm	--	--	--
Gases			
Composition, mole %			
CO	--	0.5	--
CO_2	--	88.0	--
C_1^+	--	6.5	--

Experiment No. (cont.)	158	159	160	161
Sample	BM-5	BM-5	BM-5	BM-5
Conditions				
Sample Weight, g			9.20	8.66
Temperature, °C	250	250	300	300
Residence Time, min.	0	5	0	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/15	H_2O/15	H_2O/15	H_2O/15
Special Conditions	Short Residence Time Experiments			
Mass Loss, %				
As Water	--	--	--	--
As Water Solubles	--	--	--	--
As Gas	--	--	--	--
Total	14.6	18.5	24.9	29.4
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	--	--	--	--
ii) ASTM:D 3173				
a) Modification 1	26.8	23.1	19.4	17.0
b) Modification 2	26.7	21.9	20.3	18.4
iii) Equilibrium Moisture	27.3	29.5	20.2	21.7
Heating Value, J g^{-1}, dry basis	24,660	25,590	25,150	26,160
Sulfur, %, dry basis	0.3	0.3	--	0.2
Sodium, ppm, dry basis	2,400	2,200	2,200	2,300
Potassium, ppm, dry basis	530	520	530	550
Liquids				
pH	--	--	--	--
% Solubles	--	--	--	--
Na, ppm	240	300	390	350
K, ppm	6	9	15	14
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO	0	0	6.7	23.2
CO_2	100	100	90.3	56.7
C_{1+}	--	--	3.0	20.1

Experiment No. (cont.)	162	163	164	165
Sample	BM-5	BM-5	BM-5	BM-5
Conditions				
Sample Weight, g	8.79	8.69	28.46	24.33
Temperature, °C	350	350	300	300
Residence Time, min.	0	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/15	H_2O/15	Oil:H_2O/ 110:40	Oil:H_2O/ 110:40
Special Conditions	Short Residence Experiments		Light Crude	Heavy Crude
Mass Loss, %				
As Water	--	--	26.8	21.5
As Water Solubles	--	--	0.3	0.3
As Gas	--	--	4.8	4.5
Total	24.9	39.4	31.9	26.3
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water			17.5	23.6
ii) ASTM:D 3173				
a) Modification 1	36.7	13.3	10.3	9.8
b) Modification 2	24.5	15.1	9.0	9.4
iii) Equilibrium Moisture	16.2	13.2	10.0	9.6
Heating Value, J g^{-1}, dry basis	25,590	26,980	28,700	28,250
Sulfur, %, dry basis	0.1	0.3	0.2	0.5
Sodium, ppm, dry basis	2,400	2,600	--	--
Potassium, ppm, dry basis	520	600	--	--
Liquids				
pH				
% Solubles				
Na, ppm	340	340	--	--
K, ppm	26	15	--	--
Ca, ppm				
Gases				
Composition, mole %				
CO	3.1	--	--	--
CO_2	93.5	--	--	--
C_1^+	3.4	--	--	--

Experiment No. (cont.)	166
Sample	SV-6
Conditions	
Sample Weight, g	34.3
Temperature, °C	300
Residence Time, min.	5
Atmosphere	N_2
Initial Liquid/vol, mL	H_2O/150
Special Conditions	
Mass Loss, %	
As Water	11.9
As Water Solubles	2.6
As Gas	1.6
Total	16.1
Product Analyses	
Solids	
Moisture, %	
i) By Difference in Weight of Water	19.7
ii) ASTM:D 3173	
a) Modification 1	27.8
b) Modification 2	18.3
iii) Equilibrium Moisture	14.5
Heating Value, J g^{-1}, dry basis	21,060
Sulfur, %, dry basis	0.54
Sodium, ppm, dry basis	
Potassium, ppm, dry basis	
Liquids	
pH	--
% Solubles	0.6
Na, ppm	415
K, ppm	19
Ca, ppm	7
Gases	
Composition, mole %	
CO	
CO_2	

Experiment No. (cont.)	167	168	169	170
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	30.46	29.82	31.23	29.59
Temperature, °C	200	250	250	250
Residence Time, min.	60	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	7.2	11.9	12.4	--
As Water Solubles	0.9	1.2	1.2	--
As Gas	0.6	0.5	0.7	--
Total	8.7	13.6	14.3	--
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	29.9	26.2	25.9	
ii) ASTM:D 3173				
a) Modification 1	33.3	28.9	28.4	31.8
b) Modification 2	33.2	25.5	26.2	32.4
iii) Equilibrium Moisture	22.2	27.3	26.1	--
Heating Value, J g^{-1}, dry basis	26,520	26,020	24,730	--
Sulfur, %, dry basis	5,960	5,480	5,530	--
Sodium, ppm, dry basis	780	760	750	--
Potassium, ppm, dry basis				
Liquids				
pH	7.1	--	7.0	6.8
% Solubles	0.2	0.2	0.2	--
Na, ppm	150	165	175	--
K, ppm	4	3	5	--
Ca, ppm	--	3	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	171	172	173	174
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	26.24	25.61	28.69	32.55
Temperature, °C	250	275	275	300
Residence Time, min.	60	5	60	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	12.9	10.6	13.3	20.7
As Water Solubles	2.9	1.7	3.1	1.0
As Gas	0.7	1.2	2.0	1.9
Total	16.5	13.5	18.4	23.6
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	25.9	27.8	26.2	18.1
ii) ASTM:D 3173				
a) Modification 1	29.1	31.3	31.1	24.2
b) Modification 2	23.8	32.7	31.5	20.4
iii) Equilibrium Moisture	19.7	27.8	26.2	20.5
Heating Value, J g^{-1}, dry basis	25,960	27,480	27,790	26,350
Sulfur, %, dry basis	0.19	0.21	0.18	0.31
Sodium, ppm, dry basis	4,880	5,910	5,170	4,530
Potassium, ppm, dry basis	740	780	730	780
Liquids				
pH	--	6.9	7.3	--
% Solubles	0.5	0.3	0.6	0.2
Na, ppm	218	157	275	335
K, ppm	6	4	9	6
Ca, ppm	3	--	--	3
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	175	176	177	178
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	27.80	24.51	24.67	24.06
Temperature, °C	300	300	300	300
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/40 Washed Feed	H_2O/40 Washed Feed	H_2O/150 Sat. Solution
Mass Loss, %				
As Water	13.4	24.7	20.7	24.0
As Water Solubles	5.0	1.1	1.1	1.0
As Gas	1.6	2.4	2.4	1.3
Total	20.0	28.1	24.1	26.3
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	26.4	26.1	30.5	14.3
ii) ASTM:D 3173				
a) Modification 1	28.2	23.2	26.8	--
b) Modification 2	24.0	21.6	25.3	--
iii) Equilibrium Moisture	--	--	--	--
Heating Value, J g^{-1}, dry basis	25,710	--	--	--
Sulfur, %, dry basis	0.29	--	--	--
Sodium, ppm, dry basis	--	5,420	5,330	--
Potassium, ppm, dry basis	--	710	730	--
Liquids				
pH	--	--	--	6.4
% Solubles	0.9	0.6	0.6	20.0
Na, ppm	--	370	370	63,000
K, ppm	--	20	10	48,000
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	179	180	181
Sample	SV-7	SV-7	SV-7
Conditions			
Sample Weight, g	27.48	27.61	7.18
Temperature, °C	300	300	350
Residence Time, min.	5	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions	0.7 cm lumps	2 cm lumps	--
Mass Loss, %			
As Water	15.2	13.5	--
As Water Solubles	2.2	1.7	--
As Gas	2.0	1.6	--
Total	16.8	19.4	31.8
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	24.0	25.4	--
ii) ASTM:D 3173			
a) Modification 1	27.1	30.7	22.4
b) Modification 2	27.8	30.2	23.0
iii) Equilibrium Moisture	--	--	14.2
Heating Value, J g^{-1}, dry basis	27,070	27,060	28,400
Sulfur, %, dry basis	0.14	0.21	0.3
Sodium, ppm, dry basis	5,070	5,520	--
Potassium, ppm, dry basis	800	740	--
Liquids			
pH	7.1	6.9	--
% Solubles	0.4	0.3	--
Na, ppm	255	210	--
K, ppm	8	6	--
Ca, ppm			--
Gases			
Composition, mole %			
CO	--	--	--
CO_2	--	--	--
C_1^+	--	--	--

Experiment No. (cont.)	182	183	184
Sample	SV-7	SV-7	SV-7
Conditions			
Sample Weight, g	47.41	50.0	7.61
Temperature, °C	350	370	370
Residence Time, min.	60	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150
Special Conditions			
Mass Loss, %			
As Water	--	--	--
As Water Solubles	--	--	--
As Gas	--	--	--
Total	46.0	30.6	35.6
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	--	--
ii) ASTM:D 3173			
a) Modification 1	26.4	30.6	21.9
b) Modification 2	26.5	28.2	22.4
iii) Equilibrium Moisture	15.6	19.9	13.8
Heating Value, J g^{-1}, dry basis	28,760	24,360	27,750
Sulfur, %, dry basis	--	--	0.1
Sodium, ppm, dry basis	3,990	--	--
Potassium, ppm, dry basis	690	--	--
Liquids			
pH	--	--	--
% Solubles	--	--	--
Na, ppm	950	--	--
K, ppm	29	--	--
Ca, ppm			
Gases			
Composition, mole %			
CO	0.5	--	--
CO_2	90.3	--	--
C_1^+	8.0	--	--

Experiment No. (cont.)	185	186	187	188
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	50.54	7.81	30.09	27.56
Temperature, °C	370	400	300	300
Residence Time, min.	60	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/100	H_2O/250	oil:H_2O/ 110:40	oil:H_2O/ 110:40
Special Conditions			Light Crude	Light Crude
Mass Loss, %				
As Water		--	19.6	18.9
As Water Solubles		--	2.6	2.8
As Gas		--	1.7	1.6
Total	41.4	39.2	23.9	23.4
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	--	--	19.6	20.3
ii) ASTM:D 3173				
a) Modification 1	23.9	25.2	18.2	16.1
b) Modification 2	24.4	26.4	15.3	12.7
iii) Equilibrium Moisture	17.4	12.2	14.7	11.2
Heating Value, J g^{-1}, dry basis	29,260	27,290	31,620	27,740
Sulfur, %, dry basis	--	0.20	0.04	0.39
Sodium, ppm, dry basis	4,510	--	6,180	4,870
Potassium, ppm, dry basis	710	--	750	620
Liquids				
pH	--		--	--
% Solubles			0.4	0.4
Na, ppm	1,000		250	445
K, ppm	30		10	25
Ca, ppm	--		--	--
Gases				
Composition, mole %				
CO	0.04	2.0	--	--
CO_2	84.2	82.7	--	--
C_{1+}	6.2	2.9	--	--

Experiment No. (cont.)	189	190	191	192
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	30.47	30.58	29.53	29.08
Temperature, °C	300	300	300	300
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	oil:H_2O/ 100:100	oil:H_2O/ 80:100	oil:H_2O/ 70:40	oil:H_2O/ 110:40
Special Conditions	Heavy Crude	Recycled Heavy Crude	Recycled Heavy Crude	Heavy Crude
Mass Loss, %				
As Water	16.7	--	--	--
As Water Solubles	0.1	--	--	--
As Gas	--	--	--	--
Total	18.3	--	--	--
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	23.0	--	--	--
ii) ASTM:D 3173				
a) Modification 1	24.8	27.3	26.0	11.0
b) Modification 2	24.6	27.01	25.7	10.0
iii) Equilibrium Moisture	--	--	--	--
Heating Value, J g^{-1}, dry basis	27,310	28,430	28,730	30,040
Sulfur, %, dry basis	0.20	0.21	0.22	0.19
Sodium, ppm, dry basis	4,730	5,260	5,540	--
Potassium, ppm, dry basis	730	725	740	--
Liquids				
pH	--	--	--	--
% Solubles	0.6	0.8	1.1	--
Na, ppm	425	275	505	--
K, ppm	15	7	15	--
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	193	194	195	196
Sample	SV-7	SV-7	SV-7	SV-7
Conditions				
Sample Weight, g	8.93	8.48	9.72	9.95
Temperature, °C	250	250	300	300
Residence Time, min.	0	5	0	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/15	H_2O/15	H_2O/15	H_2O/15
Special Conditions	Short Residence Time Experiments			
Mass Loss, %				
As Water	--	--	--	--
As Water Solubles	--	--	--	--
As Gas	--	--	--	--
Total	17.4	16.3	23.9	23.9
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	--	--	--	--
ii) ASTM:D 3173				
a) Modification 1	20.9	27.6	24.6	22.0
b) Modification 2	20.5	25.5	24.3	22.4
iii) Equilibrium Moisture	31.7	27.4	32.3	19.2
Heating Value, J g^{-1}, dry basis	25,120	25,350	26,070	26,080
Sulfur, %, dry basis	0.1	0.2	--	0.1
Sodium, ppm, dry basis	5,470	5,230	--	5,440
Potassium, ppm, dry basis	420	395		
Liquids				
pH				
% Solubles				
Na, ppm	480	630	--	800
K, ppm	9	18	--	34
Ca, ppm				
Gases				
Composition, mole %				
CO				
CO_2				

Experiment No. (cont.)	197	198
Sample	SV-7	SV-7
Conditions		
Sample Weight, g	8.81	9.81
Temperature, °C	350	350
Residence Time, min.	0	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	H_2O/15	H_2O/15
Special Conditions	Short Residence Time Experiments	
Mass Loss, %		
As Water		
As Water Solubles		
As Gas		
Total	30.0	34.6
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	--	--
ii) ASTM:D 3173		
a) Modification 1	21.4	24.8
b) Modification 2	20.0	22.6
iii) Equilibrium Moisture	17.0	16.1
Heating Value, J g^{-1}, dry basis	23,860	27,540
Sulfur, %, dry basis	0.35	--
Sodium, ppm, dry basis	5,460	5,900
Potassium, ppm, dry basis	410	420
Liquids		
pH		
% Solubles		
Na, ppm	770	900
K, ppm	20	20
Ca, ppm		
Gases		
Composition, mole %		
CO	2.1	1.7
CO_2	91.7	91.1
C_1^+	2.9	4.1

Experiment No. (cont.)	199
Sample	SV-9
Conditions	
Sample Weight, g	28.00
Temperature, °C	300
Residence Time, min.	5
Atmosphere	N_2
Initial Liquid/vol, mL	H_2O/150
Special Conditions	
Mass Loss, %	
As Water	9.5
As Water Solubles	3.3
As Gas	1.3
Total	14.1
Product Analyses	
Solids	
Moisture, %	
i) By Difference in Weight of Water	27.9
ii) ASTM:D 3173	
a) Modification 1	35.3
b) Modification 2	35.2
iii) Equilibrium Moisture	15.9
Heating Value, J g^{-1}, dry basis	25,220
Sulfur, %, dry basis	0.23
Sodium, ppm, dry basis	
Potassium, ppm, dry basis	
Liquids	
pH	7.6
% Solubles	0.6
Na, ppm	320
K, ppm	7
Ca, ppm	--
Gases	
Composition, mole %	
CO	--
CO_2	--

Experiment No. (cont.)	200
Sample	SV-10

Conditions

Sample Weight, g	30.51
Temperature, °C	300
Residence Time, min.	5
Atmosphere	N_2
Initial Liquid/vol, mL	H_2O/150
Special Conditions	

Mass Loss, %

As Water	9.9
As Water Solubles	2.6
As Gas	1.3
Total	13.8

Product Analyses

Solids

Moisture, %	
i) By Difference in Weight of Water	29.5
ii) ASTM:D 3173	
a) Modification 1	30.1
b) Modification 2	31.1
iii) Equilibrium Moisture	--
Heating Value, J g^{-1}, dry basis	24,590
Sulfur, %, dry basis	0.27
Sodium, ppm, dry basis	
Potassium, ppm, dry basis	

Liquids

pH	7.4
% Solubles	0.5
Na, ppm	280
K, ppm	7
Ca, ppm	--

Gases

Composition, mole %	
CO	--
CO_2	--

Experiment No. (cont.)	201	202
Sample	CM-5	CM-5
Conditions		
Sample Weight, g	27.47	26.89
Temperature, °C	250	300
Residence Time, min.	5	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150
Special Conditions		
Mass Loss, %		
As Water	11.8	--
As Water Solubles	0.6	--
As Gas	0.8	1.8
Total	13.2	17.5
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	28.5	26.8
ii) ASTM:D 3173		
a) Modification 1	31.1	30.7
b) Modification 2	27.0	25.7
iii) Equilibrium Moisture	26.7	20.9
Heating Value, J g^{-1}, dry basis	22,260	23,770
Sulfur, %, dry basis	0.17	0.23
Sodium, ppm, dry basis		
Potassium, ppm, dry basis		
Liquids		
pH	--	--
% Solubles	0.1	--
Na, ppm	38	37
K, ppm	19	15
Ca, ppm	16	26
Gases		
Composition, mole %		
CO	--	--
CO_2	--	--

Experiment No. (cont.)	203
Sample	CM-6
Conditions	
Sample Weight, g	27.51
Temperature, °C	300
Residence Time, min.	5
Atmosphere	N_2
Initial Liquid/vol, mL	H_2O/150
Special Conditions	
Mass Loss, %	
As Water	18.2
As Water Solubles	0.9
As Gas	0.8
Total	19.9
Product Analyses	
Solids	
Moisture, %	
i) By Difference in Weight of Water	26.9
ii) ASTM:D 3173	
a) Modification 1	32.3
b) Modification 2	28.1
iii) Equilibrium Moisture	
Heating Value, J g^{-1}, dry basis	22,910
Sulfur, %, dry basis	0.17
Sodium, ppm, dry basis	
Potassium, ppm, dry basis	
Liquids	
pH	--
% Solubles	0.16
Na, ppm	31
K, ppm	15
Ca, ppm	21
Gases	
Composition, mole %	
CO	--
CO_2	--

Experiment No. (cont.)	204	205	206	207
Sample	CM-7	CM-7	CM-7	CM-7
Conditions				
Sample Weight, g	27.45	27.29	29.19	29.60
Temperature, °C	150	200	250	250
Residence Time, min.	60	60	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water	7.6	15.8	18.7	--
As Water Solubles	0.4	0.5	0.5	--
As Gas	0.5	1.0	1.2	--
Total	8.5	17.3	20.4	--
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	32.4	25.8	23.4	--
ii) ASTM:D 3173				
a) Modification 1	36.6	30.5	28.1	31.5
b) Modification 2	37.0	31.9	24.0	31.3
iii) Equilibrium Moisture	21.1	20.0	17.6	--
Heating Value, J g^{-1}, dry basis	24,100	25,180	22,670	--
Sulfur, %, dry basis	0.51	0.44	0.62	--
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	6.0	5.6	5.7	--
% Solubles	0.1	0.1	0.1	--
Na, ppm	28	30	31	--
K, ppm	7	7	10	--
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO	--	--	--	--
CO_2	--	--	--	--

Experiment No. (cont.)	208	209	210	211
Sample	CM-7	CM-7	CM-7	CM-7
Conditions				
Sample Weight, g	27.99	29.21	25.54	30.07
Temperature, °C	275	275	300	300
Residence Time, min.	5	60	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions	--	--	--	--
Mass Loss, %				
As Water	25.1	24.6	25.8	--
As Water Solubles	0.8	1.3	1.3	--
As Gas	1.8	2.8	2.6	--
Total	27.7	28.7	29.7	--
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	16.7	17.6	16.3	--
ii) ASTM:D 3173				
a) Modification 1	26.1	26.8	25.7	25.8
b) Modification 2	26.4	24.9	25.6	27.1
iii) Equilibrium Moisture	23.4	17.8	17.8	--
Heating Value, J g^{-1}, dry basis	25,360	24,610	23,650	--
Sulfur, %, dry basis	0.27	0.60	0.59	--
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	5.6	5.1	5.3	5.3
% Solubles	0.1	0.2	0.2	--
Na, ppm	33	34	39	--
K, ppm	10	14	12	--
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO	--	--	--	2.6
CO_2	--	--	--	94.5
	--	--	--	0.9

Experiment No. (cont.)	212	213	214	215
Sample	CM-7	CM-7	CM-7	CM-7
Conditions				
Sample Weight, g	28.91	29.95	6.45	7.45
Temperature, °C	310	310	350	370
Residence Time, min.	5	5	5	5
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/180
Special Conditions	--	--	--	--
Mass Loss, %				
As Water	27.6	27.9	--	--
As Water Solubles	1.3	0.6	--	--
As Gas	2.3	3.1	--	--
Total	31.2	31.6	34.6	36.6
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water	14.0	13.6	--	--
ii) ASTM:D 3173				
a) Modification 1	22.8	20.4	20.9	26.0
b) Modification 2	21.6	21.1	21.7	26.6
iii) Equilibrium Moisture	18.9	--	16.1	14.2
Heating Value, J g^{-1}, dry basis	24,370	24,790	25,410	27,300
Sulfur, %, dry basis	0.18	0.34	--	0.1
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	5.3	5.2	--	--
% Solubles	0.2	0.4	--	--
Na, ppm	29	78	--	--
K, ppm	15	29	--	--
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO	--	--	--	--
CO_2	--	--	--	--

Experiment No. (cont.)	216	217	218
Sample	CM-7	CM-7	CM-7
Conditions			
Sample Weight, g	7.32	28.06	26.01
Temperature, °C	400	300	300
Residence Time, min.	5	5	5
Atmosphere	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/250	oil:H_2O/ 110:40	oil:H_2O/ 100:40
Special Conditions	--	Light Crude	Heavy Crude
Mass Loss, %			
As Water	--	22.9	21.8
As Water Solubles	--	1.8	1.7
As Gas	--	2.6	1.9
Total	39.7	27.3	25.4
Product Analyses			
Solids			
Moisture, %			
i) By Difference in Weight of Water	--	19.6	20.6
ii) ASTM:D 3173			
a) Modification 1	22.4	24.7	16.7
b) Modification 2	23.6	21.5	15.8
iii) Equilibrium Moisture	4.6	17.0	14.5
Heating Value, J g^{-1}, dry basis	27,650	26,490	28,160
Sulfur, %, dry basis	0.2	0.92	0.53
Sodium, ppm, dry basis			
Potassium, ppm, dry basis			
Liquids			
pH	--	--	--
% Solubles	--	0.3	0.2
Na, ppm	--	220	270
K, ppm	--	28	28
Ca, ppm	--	--	--
Gases			
Composition, mole %			
CO	--	--	--
CO_2	--	--	--

Experiment No. (cont.)	219	220
Sample	CM-7	CM-7
Conditions		
Sample Weight, g	10.05	9.06
Temperature, °C	300	300
Residence Time, min.	0	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	H_2O/15	H_2O/15
Special Conditions	Short Residence Time	
Mass Loss, %		
As Water	--	--
As Water Solubles	--	--
As Gas	--	--
Total	27.5	31.4
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	--	--
ii) ASTM:D 3173		
a) Modification 1	24.6	22.3
b) Modification 2	24.0	17.6
iii) Equilibrium Moisture	25.6	17.5
Heating Value, J g^{-1}, dry basis	22,960	22,080
Sulfur, %, dry basis	--	--
Sodium, ppm, dry basis	--	--
Potassium, ppm, dry basis	--	--
Liquids		
pH	--	--
% Solubles	--	--
Na, ppm	90	60
K, ppm	28	26
Ca, ppm	--	--
Gases		
Composition, mole %		
CO	5.0	--
CO_2	92.0	--
C_1^+	3.0	--

Experiment No. (cont.)	221	222	223	224
Sample	PM-3	PM-3	PM-3	PM-3
Conditions				
Sample Weight, g	10.0	10.0	10.0	58.7
Temperature, °C	250	300	350	370
Residence Time, min.	5	5	5	60
Atmosphere	N_2	N_2	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/150	H_2O/150	H_2O/150
Special Conditions				
Mass Loss, %				
As Water				
As Water Solubles				
As Gas				
Total				
Product Analyses				
Solids				
Moisture, %				
i) By Difference in Weight of Water				
ii) ASTM:D 3173				
a) Modification 1	83.1	81.5	26.8	63.1
b) Modification 2	78.6	80.8	34.8	61.5
iii) Equilibrium Moisture	20	35	29.2	11.7
Heating Value, J g^{-1}, dry basis	27,050	28,620	27,250	29,180
Sulfur, %, dry basis	--	0.5	--	0.3
Sodium, ppm, dry basis				
Potassium, ppm, dry basis				
Liquids				
pH	--	--	--	--
% Solubles	--	--	--	--
Na, ppm	110	70	160	110
K, ppm	36	25	71	10
Ca, ppm	--	--	--	--
Gases				
Composition, mole %				
CO	--	--	--	0
CO_2	--	--	--	99

Experiment No. (cont.)	225	226
Sample	PM-3	PM-3
Conditions		
Sample Weight, g	50	8.79
Temperature, °C	370	400
Residence Time, min.	5	5
Atmosphere	N_2	N_2
Initial Liquid/vol, mL	H_2O/150	H_2O/250
Special Conditions		
Mass Loss, %		
As Water	--	--
As Water Solubles	--	--
As Gas	--	--
Total	88.8	85.2
Product Analyses		
Solids		
Moisture, %		
i) By Difference in Weight of Water	--	--
ii) ASTM:D 3173		
a) Modification 1	62.3	55.2
b) Modification 2	59.9	54.2
iii) Equilibrium Moisture	10.7	5.7
Heating Value, J g^{-1}, dry basis	28,650	31,430
Sulfur, %, dry basis	0.2	--
Sodium, ppm, dry basis	--	--
Potassium, ppm, dry basis	--	--
Liquids		
pH	--	--
% Solubles	--	--
Na, ppm	--	--
K, ppm	--	--
Ca, ppm	--	--
Gases		
Composition, mole %		
CO	--	--
CO_2	--	--

APPENDIX C

Analytical Data for Selected Original Samples and Solid Products of Thermal Dewatering

Sample (Experimental Conditions)	Moisture %	Equilibrium Moisture %
ON-4 (original sample)	46.5	41.8
ON-4 (300°C)	28.1	17.4
BM-5 (original sample)	32.1	31.9
BM-5 (300°C)	26.9	18.0
BM-5 (370°C)	19.6	18.8
SV-7 (original sample)	34.5	33.4
SV-7 (300°C)	22.2	20.0
SV-7 (370°C)	25.6	17.1
SV-7 (300°C, light crude oil)	14.0	13.2
SV-7 (300°C, heavy crude oil)	10.0	--
PM-3 (original sample)	83.0	72.0
PM-3 (370°C)	61.5	10.7

Sample (Experimental Conditions) (cont.)	Proximate Analysis, % (dry basis) Ash	Volatiles	Fixed Carbon (by diff.)
ON-4 (original sample)	18.2	41.0	40.8
ON-4 (300°C)	10.4	39.3	50.3
BM-5 (original sample)	9.2	42.8	48.0
BM-5 (300°C)	9.6	36.3	54.1
BM-5 (370°C)	10.7	26.1	63.2
SV-7 (original sample)	10.7	40.9	48.4
SV-7 (300°C)	10.4	36.7	52.9
SV-7 (370°C)	10.4	24.1	65.5
SV-7 (300°C, light crude oil)	10.4	--	--
SV-7 (300°C, heavy crude oil)	9.9	43.2	46.9
PM-3 (original sample)	4.5	--	--
PM-3 (370°C)	12.8	--	--

Sample (Experimental Conditions) (cont.)	Ultimate Analysis, % (dry basis) C	H	N	S	Ash	O (by diff.)
ON-4 (original sample)	57.2	4.6	0.5	0.6	18.2	18.9
ON-4 (300°C)	65.0	5.0	0.5	1.1	10.4	18.0
BM-5 (original sample)	64.6	5.3	1.1	0.7	9.2	19.1
BM-5 (300°C)	66.7	5.5	1.1	0.6	9.6	16.5
BM-5 (370°C)	71.3	4.6	1.2	0.5	10.7	11.7
SV-7 (original sample)	63.6	5.3	1.1	0.4	10.7	18.9
SV-7 (300°C)	65.3	5.2	1.1	0.4	10.4	17.6
SV-7 (370°C)	70.7	4.7	1.2	0.3	10.4	12.7
SV-7 (300°C, light crude oil)	68.0	5.6	1.1	0.4	10.4	14.5
SV-7 (300°C, heavy crude oil)	69.1	6.0	1.1	0.7	9.9	13.2
PM-3 (original sample)	55.4	6.5	1.9	0.2	4.5	31.5
PM-3 (370°C)	--	--	--	--	--	--

Sample (Experimental Conditions) (cont.)	Na, ppm (dry basis) (by acid digestion) (± 400)
ON-4 (original sample)	890
ON-4 (310°C)	220
ON-4 (310°C, repeat[1])	200
BDM-6 (original sample)	4,100
BDM-6 (300°C)	2,100
BM-5 (original sample)	2,900
BM-5 (original sample, repeat[1])	3,800
BM-5 (300°C)	3,100
BM-5 (350°C)	1,600
SV-7 (original sample)	6,800
SV-7 (original sample, repeat[1])	4,700
SV-7 (300°C)	5,600
SV-7 (300°C, repeat[1])	5,800
CM-7 (original sample)	200 ± 30
CM-7 (300°C)	600 ± 30
CM-7 (310°C)	100 ± 30

[1] Repeat analyses by same outside laboratory, but at different date and on different sample.

Sample (Experimental Conditions) (cont.)	Hardgrove Grindability Index	Free Swelling Index
BM-5 (original sample)	18	0
BM-5 (300°C)	51	0
SV-7 (original sample)	33	0
SV-7 (300°C)	69	0

Sample (Expt'd Conditions) (cont.)	Bulk Density g mL^{-1}	Apparent Specific Gravity (± 0.05)	True Specific Gravity (± 0.05)	Porosity (± 4)%
ON-4 (original sample)	0.510	1.25	1.66 ?	25 ?
ON-4 (250°C)	0.605	--	--	--
ON-4 (300°C)	0.564	1.17	1.48	20 ?
BM-5 (original sample)	0.650	1.27	1.53	17
BM-5 (300°C)	0.605	1.19	1.51	21
BM-5 (370°C)	0.588	--	--	--
SV-7 (original sample)	0.682	1.28	1.50	15
SV-7 (200°C)	0.707	--	--	--
SV-7 (250°C)	0.643	--	--	--
SV-7 (300°C)	0.617	1.17	1.49	21
SV-7 (370°C)	0.602	--	--	--
SV-7 (300°C, heavy crude oil)	0.577	--	--	--
CM-7 (original sample)	0.639	--	--	--
CM-7 (250°C)	0.565	--	--	--
CM-7 (300°C)	0.617	--	--	--
CM-7 (300°C, heavy crude oil)	0.779	--	--	--

Sample (Expt'l Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm)					
	Ag	Al	B	Ba	Be	Ca
ON-4 (original sample)	0.89	4,600	43	81	<0.1	14,700
ON-4 (300°C)	1.0	6,300	2.0	86	<0.1	13,200
BM-5 (original sample)	3.0	10,000	130	460	<0.1	17,000
BM-5 (300°C)	2.0	9,200	75	560	<0.1	18,300
BM-5 (370°C)	1.0	9,500	21	540	<0.1	22,800
SV-7 (original sample)	1.6	10,200	120	670	<0.1	11,800
SV-7 (300°C)	4.0	10,400	15,700(?)	270	<0.1	13,800
SV-7 (370°C)	1.0	11,400	50	320	<0.1	16,600
SV-7 (300°C, light crude oil)	2.0	8,600	110	180	<0.1	11,300
SV-7 (300°C, heavy crude oil)	2.0	9,000	70	340	<0.1	12,400
PM-3 (original sample)	0.2	2,700	44	91	<0.1	6,600
PM-3 (370°C)	40	7,400	77	320	<0.1	12,000

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm)					
	Cd	Co	Cr	Cu	Fe	K
ON-4 (original sample)	<0.1	2.0	0.4	11	2,400	280
ON-4 (300°C)	<0.1	4.0	7.0	36	6,900	130
BM-5 (original sample)	<0.1	2.0	5.0	62	3,200	190
BM-5 (300°C)	0.4	2.0	5.0	71	3,900	150
BM-5 (370°C)	0.2	2.0	4.0	200	4,400	170
SV-7 (original sample)	0.4	5.0	9.0	23	3,100	270
SV-7 (300°C)	0.2	6.0	10	24	3,600	500
SV-7 (370°C)	1.0	6.0	99	560	4,400	240
SV-7 (300°C, light crude oil)	4.9	5.9	10	25	3,300	200
SV-7 (300°C, heavy crude oil)	2.0	5.0	7.0	19	3,200	150
PM-3 (original sample)	0.3	8.0	4.0	12	1,500	130
PM-3 (370°C)	<0.1	4.0	12	17,200(?)	4,000	280

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm)					
	Mg	Mn	Mo	Na	Ni	P
ON-4 (original sample)	2,800	17	<0.1	1,500	13	61
ON-4 (300°C)	3,000	32	<0.1	440	9.0	130
BM-5 (original sample)	2,600	15	<0.1	4,200	<0.1	530
BM-5 (300°C)	2,900	15	<0.1	3,500	5.0	590
BM-5 (370°C)	3,700	19	<0.1	2,200	6.0	710
SV-7 (original sample)	2,100	9.9	<0.1	6,700	12	110
SV-7 (300°C)	2,200	12	<0.1	4,200	15	82
SV-7 (370°C)	2,800	15	<0.1	3,100	16	99
SV-7 (300°C, light crude oil)	2,100	13	<0.1	5,100	17	75
SV-7 (300°C, heavy crude oil)	2,000	11	<0.1	4,600	11	65
PM-3 (original sample)	680	56	<0.1	400	3.0	550
PM-3 (370°C)	1,900	140	<0.1	150	34	1,300

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm) Pb	Si	Ti	V	W	Zn
ON-4 (original sample)	<0.1	180	43	7.0	<1.0	32
ON-4 (300°C)	<0.1	110	120	12	<1.0	59
BM-5 (original sample)	9.0	180	310	6.0	<1.0	26
BM-5 (300°C)	<1.0	95	350	7.0	<1.0	42
BM-5 (370°C)	<1.0	640	410	80	<1.0	59
SV-7 (original sample)	<1.0	180	200	18	<1.0	42
SV-7 (300°C)	<1.0	110	210	16	<1.0	680
SV-7 (370°C)	<1.0	120	210	17	<1.0	50
SV-7 (300°C, light crude oil)	<1.0	140	170	10	<1.0	68
SV-7 (300°C, heavy crude oil)	<1.0	54	150	13	<1.0	22
PM-3 (original sample)	20	57	33	6.0	<1.0	31
PM-3 (370°C)	7.0	200	100	15	<1.0	150

APPENDIX D

Analytical Data for Selected Aqueous Products of Thermal Dewatering

Sample (Experimental Conditions)	Yield, Aqueous Product[1] mL g^{-1} dry weight sample	Solubles %	pH
ON-4 (300°C)		1.4	5.4
BM-5 (300°C)	9.1	1.3	6.9
BM-5 (370°C)	4.3	--	--
SV-7 (300°C)	8.6	2.1	7.0
SV-7 (370°C)	4.8	--	--
SV-7 (300°C, light crude oil)	2.5	2.6	--
SV-7 (300°C, heavy crude oil)	2.6	2.8	--
PM-3 (370°C)	22.6	--	--

[1] Includes water present initially.

Sample (Expt'd Conditions) (cont.)	Anion Concentrations, μg mL^{-1}				
	$S^{=}$	Cl^{-}(±0.5)	NO_3^{-}(±0.8)	$SO_4^{=}$(±1.0)	F^{-}(±0.1)
ON-4 (300°C)	21	8.3	5.5	23	1.0
BM-5 (300°C)	0.8	5.3	1.5	30	1.3
BM-5 (300°C, repeat)	18	5.6	2.5	31	1.3
BM-5 (370°C)	18	15.2	≤0.8	30	0.6
SV-7 (300°C)	36	9.7	1.8	380	2.9
SV-7 (370°C)	30	13.6	1.8	57	1.4
SV-7 (300°C, light crude oil)					
SV-7 (300°C, heavy crude oil)	19	26.5	2.8	34	3.7
PM-3 (370°C)	na	13.2	2.2	39	≤0.1

Sample (Expt'd Conditions) (cont.)	TIC µg mL^{-1}	TOC µg mL^{-1}
ON-4 (300°C)	3.2	1.7
BM-5 (300°C)	2.2	1.7
BM-5 (300°C, repeat)	2.2	1.7
BM-5 (370°C)	5.6	4.9
SV-7 (300°C)	2.5	1.9
SV-7 (370°C)	58	6.2
SV-7 (300°C, light crude oil)	--	--
SV-7 (300°C, heavy crude oil)	2.2	3.0
PM-3 (370°C)	5.6	3.6

Sample (Expt'd Conditions) (cont.)	B.O.D. $\mu g\ mL^{-1}$
SW-7 (250°C)	100 (± 5)
SW-7 (300°C)	800 (± 20)
SW-7 (370°C)	8,300 (±100)

Sample (Expt'd Conditions) (cont.)	Oxidation-Reduction Potential E_L, mV
ON-4 (250°C)	229
ON-4 (300°C)	135
SV-7 (250°C)	224
SV-7 (300°C)	246
CM-7 (250°C)	107
CM-7 (300°C)	86

Sample (Expt'l Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm) Ag	Al	B	Ba	Be	Ca
BM-4 (300°C)	<0.2	<1	9	0.1	<0.1	18
BM-5 (300°C)	0.2	<1	15	0.4	<0.1	5.5
BM-5 (300°C, repeat)	<0.2	<1	17	0.2	<0.1	1.5
BM-5 (370°C)	<0.2	<1	69	0.4	<0.1	140
SV-7 (300°C)	<0.2	1	11	0.2	<0.1	2.5
SV-7 (370°C)	<0.2	<1	61	0.2	<0.1	120
SV-7 (300°C, heavy crude oil)	<0.2	5	17	0.3	<0.1	<0.5
PM-3 (370°C)	<0.2	<1	17	1.0	<0.1	280
PM-3 (370°C, duplicate)	<0.2	<1	11	0.6	<0.1	200

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm) Cd	Co	Cr	Ca	Fe	K
ON-4 (300°C)	<0.1	<0.1	<0..2	<0.1	<0.1	5
BM-5 (300°C)	<0.1	<0.1	<0.2	0.3	<0.1	5
BM-5 (300°C, repeat)	<0.1	<0.1	<0.2	0.2	<0.1	<5
BM-5 (370°C)	<0.1	<0.1	<0.2	0.2	<0.1	25
SV-7 (300°C)	<0.1	<0.1	<0.2	0.4	8.5	15
SV-7 (370°C)	<0.1	<0.1	<0.2	<0.1	<0.1	15
SV-7 (300°C, heavy crude oil)	<0.1	<0.1	<0.2	<0.1	<0.1	<5
PM-3 (370°C)	<0.1	<0.1	<0.2	<0.1	2.1	10
PM-3 (370°C, duplicate)	<0.1	<0.1	<0.2	<0.1	<0.1	5

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm)					
	Mg	Mn	Mo	Na	Ni	P
ON-4 (300°C)	5	<0.1	<0.1	62	<0.1	<5
BM-5 (300°C)	2	<0.1	<0.1	150	<0.1	5
BM-5 (300°C, repeat)	<1	<0.1	<0.1	200	<0.1	<5
BM-5 (370°C)	5	<0.1	<0.1	680	<0.1	5
SV-7 (300°C)	2	<0.1	<0.1	280	<0.1	<5
SV-7 (370°C)	3	<0.1	<0.1	1,100	<0.1	<5
SV-7 (300°C, heavy crude oil)	<1	<0.1	<0.1	380	<0.1	<5
PM-3 (370°C)	<1	<0.1	0.3	110	<0.1	<5
PM-3 (370°C, duplicate)	<1	<0.1	<0.1	81	<0.1	<5

Sample (Expt'd Conditions) (cont.)	Trace Element Analyses (ICP-AES, ppm) Pb	Si	Ti	U	V	W	Zn
ON-4 (300°C)	<1	11	<0.1	<2	<0.1	<1	<0.1
BM-5 (300°C)	<1	13	<0.2	<2	<0.1	<1	<0.1
BM-5 (300°C, repeat)	<1	11	<0.1	<2	<0.1	<1	<0.1
BM-5 (370°C)	<1	110	<0.1	<2	<0.1	<1	<0.1
SV-7 (300°C)	<1	24	<0.1	<2	<0.1	<1	<0.1
SV-7 (370°C)	<1	100	<0.1	<2	<0.1	<1	<0.1
SV-7 (300°C, heavy crude oil)	<1	23	<0.1	<2	<0.1	<1	<0.1
PM-3 (370°C)	<1	53	<0.1	<2	<0.1	<1	<0.1
PM-3 (370°C, duplicate)	<1	38	<0.2	<2	<0.1	<1	<0.1

APPENDIX E

Averaged Data for Selected Solid Products of Thermal Dewatering

Experiment No.	105-8	146-149	154	173-175
Sample	ON-4	BM-5	BM-5	SV-7
Conditions				
Temperture, °C	300	300	300	300
Residence Time, min.	5	5	5	5
Special conditions	--	--	--	--
Moisture, %	28.1	21.9	19.6	22.2
Eq. Moisture, %	17.4	--	18.8	20.5
Analytical Data, Dry Basis				
Proximate Analysis, %				
Ash	11.1	9.5	--	11.3
Volatile Matter	39.3	36.3	--	36.7
Fixed Carbon	49.6	54.2	--	52.0
Heating Value, J g^{-1}	26,060	26,390	28,660	26,220
Ultimate Analyses				
Carbon	--	--	--	--
Hydrogen	--	--	--	--
Nitrogen	--	--	--	--
Sulphur	0.6	--	--	0.3
Ash	11.1	--	--	--
Oxygen (by diff.)	--	--	--	--
Bulk Density, g mL^{-1}	0.56	0.61	--	0.62

Experiment No.	185	187	188	225
Sample	SV-7	SV-7	SV-7	PM-3
Conditions				
Temperture, °C	370	300	300	370
Residence Time, min.	60	5	5	5
Special conditions	--	Light Crude	Heavy Crude	
Moisture, %	24.4	15.3	12.7	59.9
Eq. Moisture, %	17.4	14.7	11.2	10.7
Anaiytical Data, Dry Basis				
Proximate Analysis, %				
Ash	10.5		9.1	
Volatile Matter	24.1		43.2	
Fixed Carbon	65.4		47.7	
Heating Value, J g^{-1}	29,260	31,620	27,740	28,650
Ultimate Analyses				
Carbon	--	--	--	--
Hydrogen	--	--	--	--
Nitrogen	--	--	--	--
Sulphur	--	0.1	0.4	0.2
Ash	--	--	--	--
Oxygen (by diff.)	--	--	--	--
Bulk Density, g mL^{-1}	0.60			

APPENDIX F

Calculation of Diffusion Data for Lignite Particles

In the proposed approach, we show that the experimental data in Table 4.1.2 can be correlated to a theoretical solution for diffusion controlled adsorption of water by lignite particles. Figure 4.1.1 presents the theoretical curve and experimental data in terms of dimensionless time (Θ) and fractional conversion (w_t/w_∞) which are described below.

We start with a description of the problem and of the assumptions. It is assumed that at the end of each run (before cooling) the lignite particles contain the equilibrium concentration of moisture, equal to 16.5 percent for Onakawana lignite. The adsorption of water would then occur during a cooling period of 30 minutes. Since the adsorption of water is diffusion controlled, the amount of water adsorbed would be proportional to the time and the diffusion coefficient, and inversely proportional to the particle radius.

In terms of dimensionless variables Θ and w_t/w_∞, the amount adsorbed is described by equation (1):

$$\frac{w_t}{w_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2\Theta) \qquad (1)$$

where $\Theta = \left(\frac{Dt}{R^2}\right)^{1/2}$

D = diffusion coefficient, cm^2/sec

t = time, sec

R = particle radius, cm

w_t = moisture adsorbed by particle at time t

w_∞ = moisture adsorbed by a saturated particle at $t = \infty$

A detailed mathematical development for the unsteady mass transfer is given by J. Crank, "Mathematics of Diffusion", Oxford Press (1956).

From the experimental data in Table 4.1.2, the fractional moisture (w_t/w_∞) can be calculated directly using the formula:

$$\frac{w_t}{w_\infty} = \frac{m_t - m_{equilibrium}}{m_\infty - m_{equilibrium}} \qquad (2)$$

where m_t = moisture (%) of particle at time t

m_∞ = moisture (%) of saturated particle at $t = \infty$

To proceed further, we must determine what is the value for m_∞. It seems reasonable to assume that the particle of radius R = 0.2 cm would be saturated after 30 minutes. This would require that $D \geq 2.2 \times 10^{-5}$, which is of the order of diffusion coefficients for liquids. We can ther. write equation (2) as:

$$\frac{w_t}{w_\infty} = \frac{m_t - 16.5}{32.2 - 16.5} = \frac{m_t - 16.5}{15.7} \qquad (2A)$$

and define $D = 2.2 \times 10^{-5}$ cm^2/sec.

Table F1 presents the calculated values of w_t/w_∞, and Θ.

Table F1. VARIATION OF FRACTIONAL MOISTURE WITH DIMENSIONLESS TIME FOR VARIOUS PARTICLE SIZES

R	m_t	w_t/w_∞	Θ
0.2	32.2	1.00	1.00
0.5	28.1	0.87	0.40
0.7	27.6	0.71	0.28
2.0	24.6	0.31	0.10

The values from Table F1 were plotted in Figure 4.1.1, indicating that the experimental moisture values can be well correlated by a theoretical solution for adsorption of water controlled by the diffusion within the particle.

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